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Supercritical Fluid Extraction-Gas Chromatography of Volatile Organic Compounds (VOC) from Tenax Devices

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SUPERCRITICAL FLUID EXTRACTION-GAS CHROMATOGRAPHY OF VOLATILE ORGANIC COMPOUNDS (VOC) FROM TENAX DEVICES

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This report describes the development and evaluation of on-line supercritical fluid extraction-gas chromatography instrumentation and methodology for the analysis of volatile organic compounds (VOC) from adsorbent sampling devices. Supercritical fluid extraction offers potential advantages for the removal and transport of organic components from adsorbent matrices including rapid and efficient extraction at mild temperatures. Extraction at mild temperatures eliminates potential problems such as analyte decomposition that can be encountered with the high temperatures needed for thermal desorption analysis. Since a major objective of this study was to develop viable instrumentation and methodology, a relatively detailed description of the instrumentation design requirements and present limitations are discussed. The results of several series of methodology validation studies are also presented. These studies included recovery studies of model VOC spiked on three types of Tenax® sampling devices including authenic actively pumped (VOST) and passive (EPA) devices. Replicate devices spiked in an exposure chamber were also subjected to parallel analyses using this new methodology and traditional thermal desorption gas chromatography.

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature of processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems for air, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

The determination of human exposure to toxic organic compounds is an area of increasing importance to EPA. As analytical methodologies have become increasingly more sophisticated to allow determination of lower levels of these compounds, significant problems and limitations have become apparent. Use of supercritical fluids as extraction solvents has significant potential for extending current analytical methodologies and offering alternative approaches to overcome these limitations. This report summarizes recent work in the development of such supercritical fluid-based analytical methodology.

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ABSTRACT

This report describes the development and evaluation of on-line supercritical fluid extraction-gas chromatography instrumentation and methodology for the analysis of volatile organic compounds (VOC) from adsorbent sampling devices. Supercritical fluid extraction offers potential advantages for the removal and transport of organic components from adsorbent matrices. The liquid-like solvating power, high diffusivity, and low viscosity of a supercritical fluid provide the potential for rapid and efficient extraction rates. By utilizing a fluid with a low critical temperature, such as carbon dioxide (T_c=31°C), extractions can be conducted at mild temperatures. This eliminates the potential for any thermally induced problems such as analyte decomposition or artifact formation that can be encountered with the high temperatures needed in thermal desorption methods. Preliminary qualitative application of the methodology to less volatile compounds was also demonstrated using PCB's.

The instrumentation consisted of a high pressure fluid supply, a heated high pressure extraction cell for each type of sampling device, an interface region for depressurization of the extraction effluent, and a capillary column gas chromatograph with analyte focusing and concentration capabilities and a flame ionization detector. Due to the large volume of gas from the expanded fluid that was passed through the chromatographic column, the appropriate interface design and highly efficient analyte focusing and concentration methods were crucial. It was also necessary to use very pure carbon dioxide to prevent concentration of contaminants. A standard VOC mixture covering a limited volatility and polarity range were spiked at levels ranging between 50 and 500 ng on three types of Tenax® sampling devices. The three sampling devices consisted of a 3" x 1/4" o.d. stainless steel tube, a standard VOST tube, and a passive sampling device. Spherocarb® proved unsuitable as an adsorbent in a preliminary evaluation due to persistent high levels of contaminants that were extracted from the matrix.

Recovery studies on sampling devices spiked with known quantities of the VOC standards indicated essentially quantitative extraction and recovery could be obtained with the on-line supercritical fluid extraction-gas chromatography methodology. Extraction times generally ranged between ten and thirty minutes. The larger VOST devices required larger extraction fluid volumes (longer extraction times) which impaired efficient analyte focusing and degraded the chromatographic separations. Poorer chromatographic separations resulted in greater quantitative uncertainty due to potential overlapping contaminant components.

The results from parallel analyses of replicate devices spiked in an exposure chamber and subjected to this methodology and thermal desorption gas chromatography were ambiguous. The devices spiked in the exposure chamber were not previously cleaned by supercritical fluid extraction and when they were subjected to analysis using this methodology, contamination and coeluting compounds prevented accurate quantification of the VOC.

This report was submitted in fullfillment of contract number 68-021-4127 by Battelle Memorial Institute under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from November 1, 1985 to September 30, 1986, and work was completed as of September 30, 1986.

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SECTION 1

INTRODUCTION

The monitoring of hazardous organic vapors in ambient air is an important concern. A widely utilized approach for these determinations incorporates selective collection and concentration on adsorbent traps followed by either thermal desorption or solvent extraction. For the determination of volatile organic compounds (VOC), sample collection on Tenax-GC® followed by thermal desorption and gas chromatographic analysis is generally employed (1). Although some studies suggest that decomposition of analytes and artifact formation can occur during collection (2), these methods have been widely used and have provided generally satisfactory performance. However, it has become clear as more experience has been gained that severe problems such as analyte decomposition, analyte reactivity, artifact formation, and nonquantitative recoveries can be encountered during the thermal desorption step. These problems can be especially acute for analytes requiring high desorption temperatures (>300°C) and actually limits the volatility range of components that can be successfully desorbed from Tenax®. For instance, 1,1,1-trichloroethane (methyl chloroform) is known to decompose at higher temperatures and undergo dehydrohalogenation during thermal desorption from Tenax®.

Supercritical fluid extraction provides an alternative approach for the removal and transport of organic compounds from adsorbent materials which can be both efficient and thermally mild. The potential advantages of supercritical fluid extraction accrue from the properties of a solvent at temperatures and pressures above its critical point. At elevated pressure this single phase will have properties which are intermediate between those of the gas and liquid phases (3). The compressibility of supercritical fluids is large and densities typically 10^2 to 10^3 times greater than of the gas are obtained. Consequently, molecular interactions increase due to shorter intermolecular distances and solvating characteristics approaching those of the liquid are achieved. However, high diffusion coefficients and low viscosities similar to those of the gas are retained which provide the potential for rapid and efficient extraction rates (4). By choosing a fluid with a low critical temperature (T_c), such as carbon dioxide (T_c=31°C), extractions can be carried out at mild temperatures to alleviate any thermally induced problems. Supercritical fluid extraction also provides the potential for removal of less volatile compounds which would require excessively high temperatures for thermal desorption. The combination of on-line

supercritical fluid extraction with capillary gas chromatography (5) instrumentally links the extraction and analysis steps and allows the extraction effluent to be directly analyzed. Since this process allows the collection and concentration of trace level analytes at the head of a capillary column, high resolution and high sensitivity analyses can be obtained.

This report describes the development and an initial evaluation of on-line supercritical fluid extraction-gas chromatography (SFE-GC) methodology for the analysis of volatile organic compounds (VOC) from adsorbent sampling devices. This was the first investigation conducted to specifically address such an approach for VOC analysis and essentially no previous studies or reports exist relevant to such an analytical approach. This project included the development of appropriate instrumentation and methodology, evaluation and quantitative validation of the methodology using small sampling devices spiked with VOC standard compounds, and application of the developed methodology to actual passive air sampling devices (PSD) and actively pumped devices. Tenax® was primarily used as the adsorbent in these studies, but some initial evaluations utilizing Spherocarb® were also conducted. In addition to the evaluation studies, the instrumentation and methodology is described in detail and its present limitations discussed.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions can be drawn as a result of the studies conducted during this project:

- The general concept of combined on-line supercritical fluid extraction-gas chromatography proved viable for the quantitative extraction, recovery, concentration, and analysis of standard volatile organic compounds that were spiked on Tenax® sampling devices.
- Relatively clean blank SFE-GC analyses could be obtained from Tenax® sampling devices, but high levels of contamination from Spherocarb® sampling devices persisted even after prolonged conditioning with supercritical fluid extraction. Consequently, only Tenax® sampling devices were subjected to detailed evaluation.
- Carbon dioxide at temperatures of 50° to 75°C and a pressure of 125 bar provided adequate solvating power to extract the range of volatile organic compounds utilized in these studies from the Tenax® sampling devices.
- Quantitative extraction of the analytes from the sampling devices required several fluid volumes of the device to be utilized. Consequently, large volumes of gas from the depressurized carbon dioxide (several liters) were required to be passed through the chromatographic column. This requirement imposed specific instrumental constraints which are summarized below:
    - Minimum dead-volume construction of the sampling device extraction cells was required to minimize extraction fluid volumes.
    - Ultrapure carbon dioxide was necessary to prevent concentration of impurities.
    - A wide-bore (O.53 mm i.d.) chromatographic column was needed to provide maximum gas flow and maintain high chromatographic separation efficiency for the sampling devices examined in this work.
    - The high gas flow rate and volume impaired efficent analyte concentration which required extreme focusing methods of whole column cyrotrapping at -50°C with a thick-filmed (5 µm) stationary phase and a 15 m long retention gap.

- Tremendous differences in the instrument calibration were obtained using valves with different seal materials. Teflon® containing valves gave significantly lower response values for all of the standard VOC compounds used in this investigation.

- Good quantitative agreement between the spike and recovery levels of the VOC were obtained for the smaller volume adsorbent devices. The larger volume sampling devices (e.g., VOST) presented greater challenges and required extraction times in excess of thirty minutes to obtain complete removal of the analytes. Longer extraction times impaired efficient chromatographic separations and less reliable quantitative recovery levels (and greater departures from the spike levels) were obtained. The broadened peaks from less efficient separations generally corresponded to greater than quantitative recoveries.

- The quantitative SFE-GC analyses of the PSD and VOST devices spiked in the exposure chamber were ambiguous due to poorly resolved compounds and coeluting contaminants that were extracted from the Tenax® matrix. However, peaks matching the appropriate retention times of the spiked VOC could be distinguished.

- No apparent physical changes or deleterious effects on the sorption behavior of the Tenax® were observed after numerous (>20) supercritical fluid extraction cycles. However, some minor caking of the adsorbent was observed after extensive exposure and supercritical fluid extraction cycles.

- Preliminary investigations suggest that extension of SFE-GC methodology to the analysis of semi-volatile materials from Tenax® sampling devices is also feasible.

Recommendations for additional studies for further improvement and evaluation of the methodology and expansion of similar research areas are listed below:

- Improved analyte trapping methods need to be developed to increase the separation efficiency for the more volatile compounds and to allow faster extraction rates without compromising the chromatographic separation quality. This could be done by using longer analytical columns, longer retention gaps (e.g., 50 m), and/or incorporation of an integral baffle zone consisting of a short length of column packed with particles of deactivated Chromosorb W® or glass beads. Smaller sampling devices would also improve overall performance but the impact upon detection limits would require study.

- With the development of improved trapping methods, faster extraction rates should be developed and the limitations on analysis speed defined. For smaller volume devices, extraction times of five minutes should be conceivable.

- Additional quantitative studies should be done using rigorously prepared (purchased) standard mixtures for adsorbent exposure and instrument calibration. Improved quantitative reliability could also be obtained by utilization of a mass selective detector (MSD) to eliminate potential interferences from coeluting contaminants. These studies should also include VOC compounds that present problems for thermal desorption analyses.

- The extraction cells for the sampling devices should be redesigned to use stainless steel O-rings rather than the present polymer O-rings to eliminate the possibility of organic contaminants being leached from the O-rings.

- A rigorous investigation for the extension of SFE-GC methodology to the analysis of semi-volatile materials from adsorbent sampling devices should be conducted and the range of compounds that could be analyzed from a single analysis defined (including detection utilizing an MSD). In addition to Tenax®, such a study could include the evaluation of other adsorbent materials. For instance, Spherocarb®, or another carbon molecular sieve material that was properly purified (perhaps using supercritical fluid extraction with a highly solvating fluid) could be utilized.

- A related study on the effects of supercritical fluid extraction on the sorbent properties of the utilized adsorbents (e.g., Tenax® and perhaps Spherocarb®) should be conducted. Such a study would include rigorous evaluation of the retention volumes of selected standard VOC compounds on adsorbents exposed to various supercritical fluid extraction conditions (e.g., fluids, densities, exposure times).

- Sampling devices optimized for the SFE-GC methodology should be designed and evaluated.

SECTION 3

MATERIALS AND METHODS

SAMPLING DEVICES AND ADSORBENTS

Three types of sampling devices and two solid adsorbents were utilized in these investigations. The preliminary studies utilized small sampling devices constructed of 1/4" o.d. x 3 1/4" length stainless steel tubes fitted with 1/4" to 1/16" Swagelok® HPLC column end fittings containing 5 μm pore frits. These devices were then filled with either ~300 mg of Tenax®, 80/100 mesh, (Alltech, Chicago, IL) or ~1 g of Spherocarb®, 80/100 mesh, (Analabs, No. Haven, CT) adsorbents. The adsorbent-containing sampling devices were pre-cleaned by mild thermal conditioning at 300°C for twelve hours with a flow of ultrapure nitrogen. Authentic active and passive sampling devices containing Tenax® as the adsorbent were also utilized. The active devices were standard VOST (volatile organic sampling train) tubes containing 2 g of Tenax ® and the passive devices were the high sampling rate EPA-PSDs (Environmental Protection Agency passive sampling device) containing 400 mg of Tenax® (Scientific Instrumentation Specialists, Moscow, ID). These devices were also cleaned by mild thermal conditioning.

STANDARD COMPOUNDS AND ADSORBENT SPIKING

Several volatile organic compounds were chosen to cover a limited range of volatility and polarity. They included chloroform, 1,1-dichloroethane, 1,1,1-trichloroethane (methyl-chloroform), benzene, 2-bromopentane, and chlorobenzene. Two of these compounds, 1,1,1-trichloroethane and 2-bromopentane were chosen since they are prone to dehydro-halogenation (forming the corresponding olefin) during thermal desorption (6). Fifteen tetra-, penta-, hexa-, hepta-, and octachloro- biphenyl congeners were used for a standard mixture of semi-volatile compounds.

Standard Mixture Preparation

Standard mixtures of the VOC compounds were prepared by standard dilution techniques. In general, 10 μl of each standard VOC compound was injected into a 500 mL glass sampling

bulb that had been purged and filled to ambient pressure with high purity helium. After equilibration at 50°C for at least one hour, 0.5 to 4.0 mL aliquots of the gas mixture were withdrawn and injected into a 1000 mL glass sampling bulb that had been filled to ambient pressure with high purity helium. After equilibration of this mixture at 50°C for at least one hour, aliquots of this gas mixture were withdrawn for instrument calibration or adsorbent spiking. Standards were prepared daily or after approximately 30 mL of the final mixture had been withdrawn. The 5 mL gas-tight syringe utilized in standard mixture preparation and adsorbent spiking was calibrated using typical glassware calibration techniques (7). Although the above procedure for standard gas mixture preparation was not strictly rigorous, combined errors less than ten percent would be expected.

Adsorbent Spiking

The three types of sampling devices (small stainless steel tube, VOST tube, and PSD) were spiked with the standard VOC compounds at levels ranging between 50 and 150 ng per component by introducing known volumes of the standard gas mixtures. This was done by placing the authentic active and passive devices inside their respective high pressure extraction cells (described in the next section) and connecting a vacuum source (through a liquid nitrogen trap to prevent any contamination to the devices from the vacuum source) to the exit port of the extraction cell. A septum seal was connected to the inlet port of the extraction cell and, while vacuum was being applied, a known volume of a standard gas mixture was injected onto the device through the septum. In some cases the devices were spiked through the exit of the extraction cell to allow a back-flush extraction. Care was taken to always heat and flush the syringe with high purity helium prior to use to avoid contamination. By design, the small preliminary sampling devices also functioned as their own high pressure extraction cells and did not require separate extraction cells. Prior to spiking a sampling device with the standard VOC compound mixture, a blank supercritical fluid extraction-gas chromatographic analysis was performed to verify that the device was clean.

Exposure Chamber Spiking

The authentic active and passive devices were also spiked with VOC compounds under carefully controlled conditions. This was accomplished using the atmospheric chamber facilities at Battelle Columbus Laboratories (Columbus, OH). These facilities and their operation have been previously described (8). The chamber was evacuated, flushed with Ultra Pure Air (Matheson), and loaded with the measured concentrations of 39.6 ± 0.1 ng/ 100 cm^3 1,1,1-trichloroethane, 24.8 ± 0.1 ng/ 100 cm^3 benzene, and 26.4 ± 4.6 ng/ 100 cm^3 tetrachloromethane. Clean (by thermal desorption analysis) sampling devices were then exposed

to a 100 cm^3 equivalent volume of the gas in the chamber. A total of three active and three passive devices were prepared. One active and one passive device were then analyzed by thermal desorption and gas chromatography (at Battelle Columbus) using standardized procedures (8).

The remaining samples were sealed and shipped to Battelle Northwest Laboratories (Richland, WA) for analysis by supercritical fluid extraction-gas chromatography. The active sample devices were capped with Swagelok® fittings with Teflon® ferrules, and were wrapped in aluminum foil and placed in a metal can containing activated carbon. The passive devices were placed in glass jars that were then wrapped in aluminum foil and were placed in the same can as the active devices. Additional aluminum foil was then used as a filler and the can was sealed by a friction lid.

SUPERCRITICAL EXTRACTION FLUID

Purified carbon dioxide was used for the extraction fluid in these studies. It has a critical temperature of 31°C, a critical pressure of 72.9 atmospheres, and a melting point (sublimes) of approximately -57°C at 1 bar. High purity SFC grade carbon dioxide (Scott Specialty Gases, Plumsteadville, PA) was purchased in an aluminum cylinder without an eductor tube. It was found necessary to further purify the carbon dioxide which was done by slowly transferring it as a gas to the syringe pump while passsing it through an adsorbent trap filled with activated charcoal and alumina. To achieve "clean" carbon dioxide it was necessary to reactivate the charcoal by heating at 250°C immediately prior to placing it in the trapping device.

SECTION 4

EXPERIMENTAL PROCEDURES

INSTRUMENTATION

The on-line supercritical fluid extraction-gas chromatography instrumentation consisted of three primary sections which included a high pressure syringe pump and appropriate extraction cell, an interface region for depressurization of the extraction effluent, and a gas chromatograph with a flame ionization detector. The preliminary design of the instrumentation (5) which had proven successful for qualitative analysis was significantly modified during the course of this investigation. Since a primary objective of this study was to develop functional instrumentation and valid methodology for quantitative analysis, both the initial and final instrumentation designs will be described.

Preliminary Design

A schematic diagram of the preliminary design of the on-line SFE-GC instrumentation is shown in Figure 1. A modified Varian 8500 syringe pump provided a high pressure supply of pressure-regulated carbon dioxide to the extraction cell. The extraction cell used with this instrumental design was the small sampling device constructed of 1/4" o.d. stainless steel tubing that was described in the previous Section. The extraction cell and several inches of inlet tubing (1/16" o.d.) were placed inside a thermostatically controlled heating block to control the fluid and extraction cell temperature. Extraction temperatures ranging between 50° and 75°C were utilized.

An air-actuated Rheodyne 7010 six-port switching valve was used to direct the extraction cell effluent to either the gas chromatographic column for on-column deposition and concentration of the extract or to an exterior vent to allow cleaning of the adsorbent device. Short lengths (2-4 cm) of nominally 5 μm i.d. fused silica were used as depressurization restrictors and to maintain supercritical conditions up to the point of on-column deposition or exterior venting. The decompressed gas flow rate of the extraction fluid was typically 5-10 mL/min (~5-10 μl/min fluid flow). The restrictor for the on-column deposition was mounted through a 1/16" tee to allow the gas chromatograph carrier gas to enter coaxially along the restrictor. This connection was also mounted in a heated block to control the temperature of

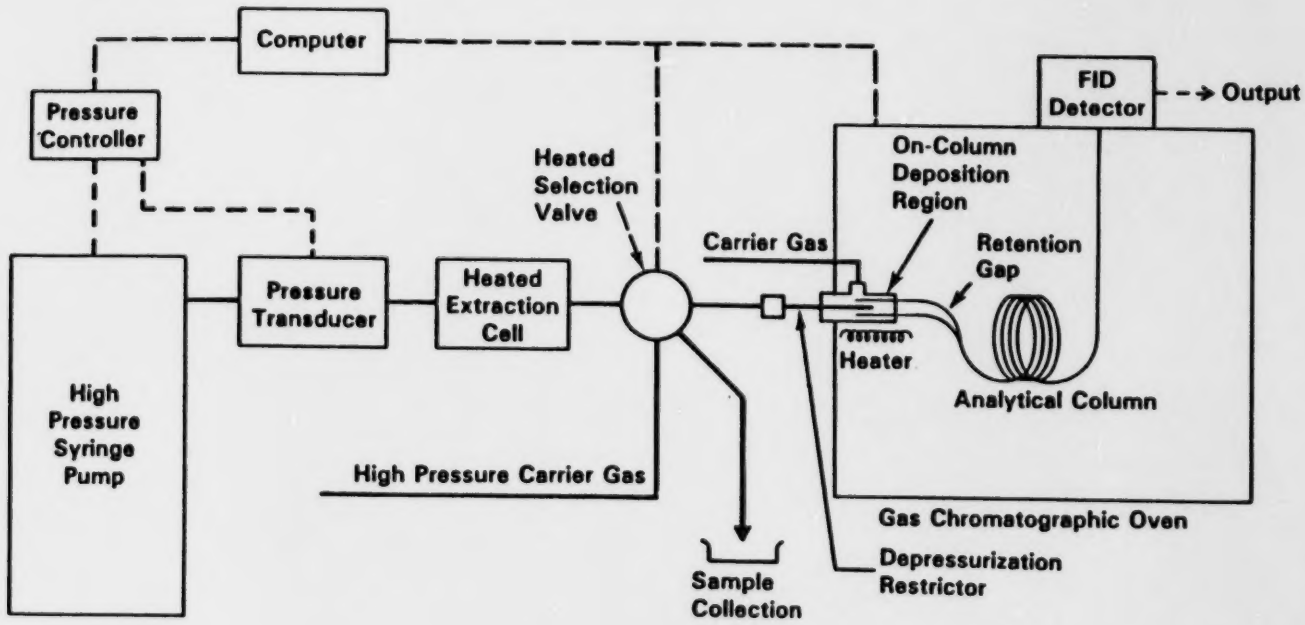

Figure 1. Schematic diagram of the preliminary design of the on-line SFE-GC instrumentation.

the restrictor and expansion region. Typically, this region was maintained near the upper operating temperature of the chromatographic oven which was 200°C. High pressure carrier gas (300 psi) was also connected to the six-port valve which flowed through the restrictor after an extraction was completed to purge any remaining effluent.

A Hewlett-Packard 5890 gas chromatograph equipped with a single flame ionization detector and liquid carbon dioxide subambient cooling was used to perform chromatographic analyses. A 30 m x 0.32 mm i.d. fused silica capillary column coated with a 5 μm film thickness of crosslinked polymethylsiloxane (DB-1, J & W Scientific, Folsom, CA) was utilized. A short retention gap of deactivated fused silica tubing (1 m x 0.25 mm i.d.) was connected to the inlet end of the chromatographic column to aid solute focusing and concentration of the extraction effluent. The fused silica retention gap was deactivated by silylation with hexamethyldisilazane at 350°C and the retention gap was connected to the analytical column with a single polyimide ferrule butt connector (Supelco, Bellafonte, PA). The chromatographic oven was lowered to 0°C during the concentration and on-column deposition of the analytes in the extraction effluent. Purified helium was used for the carrier gas at a linear velocity of approximately 30 cm/sec (~15 psi head pressure).

Final Design

A schematic diagram of the final design of the on-line SFE-GC instrumentation used in this work is shown in Figure 2. The pumping and pressure control system was the same as in the initial design. However, the interface region and the chromatographic parameters were modified to allow significantly larger extracting fluid volumes per unit time to be utilized.

The appropriate extraction cell was directly heated with a thermostated cartridge heater for more efficient heating. Extraction temperatures ranging between 50° and 75°C were utilized. The fluid entering the extraction cell was preheated to approximately 50°C by applying 5 amps of current to the final 8" of the 1/16" s.s. inlet tubing. A 1/16" high pressure on/off valve was placed immediately after the extraction cell and mounted on a heated block to maintain temperature control. Short lengths of 25 μm i.d. (4-8 cm) and tapered 50 μm i.d. fused silica were used for the depressurization restrictors which allowed much faster fluid flows ranging between approximately 100 and 350 μl/min which corresponds to approximately 100 to 350 mL/min of gas flow. Due to the increased cooling from the more rapid expansion (Joule-Thomson effect), it was necessary to have the expansion occur in a zone of higher heat capacity than fused silica to increase heat transfer to the expanding gas and prevent the extraction effluent from freezing the column closed. Consequently, a separate expansion region was constructed from a 3" length of 1/16" o.d. x 0.020" i.d. glass-lined stainless tubing (SGE,

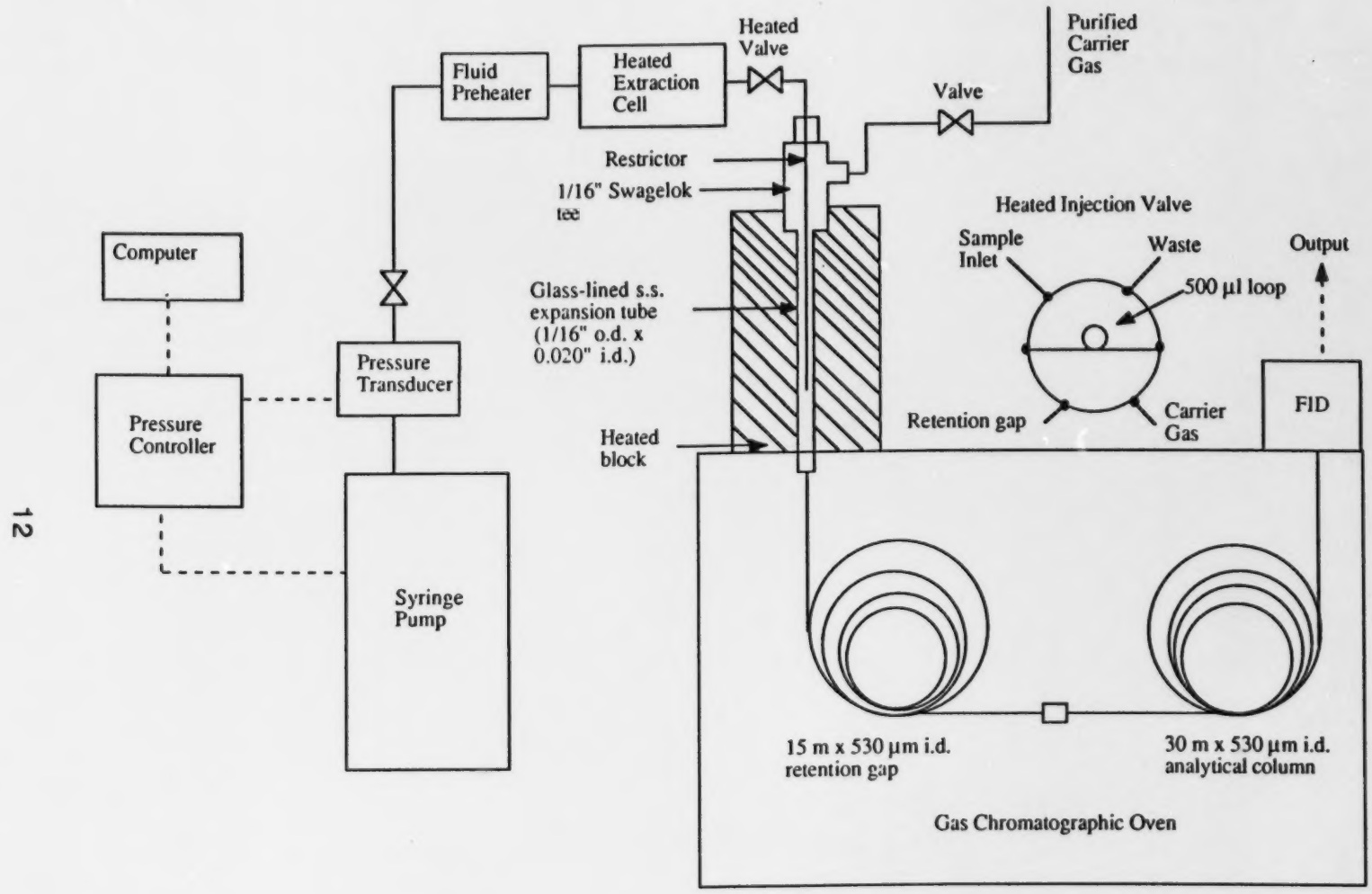

Figure 2. Schematic diagram of the final design of the on-line SFE-GC instrumentation.

Austin TX) that was tightly inserted in a metal block heated to 75°C. The restrictor was connected to the expansion tube through a 1/16" tee to allow the carrier gas to enter the expansion region coaxially along the restrictor. The heated block and expansion region were positioned outside of (and insulated from) the oven to facilitate subambient cooling of the oven.

To accommodate the much higher gas flow rate, the smaller diameter capillary column was replaced with a 30 m x 0.53 mm i.d. (larger diameter) column coated with a 5 μm film thickness of crosslinked polymethylsiloxane (DB-1, J & W Scientific, Folsom, CA). The carrier gas inlet was also valved so it could be closed during extraction (and pressure build-up) to prevent backflushing of the extraction effluent into the carrier gas inlet lines. A relatively long 15 m x 0.53 mm i.d. deactivated fused silica retention gap was connected between the heated expansion region and the analytical column to facilitate solute focusing and concentration of the extraction effluent. The retention gap was deactivated and connected to the analytical column in the same fashion as described for the preliminary instrumentation design. Whole column cryotrapping (9,10) of the extraction effluent was accomplished by lowering the chromatographic oven temperature to -50°C during extraction. Purified helium was used as a carrier gas at a linear velocity of 40 cm/sec (~6 psi head pressure).

Extraction Cells

Three types of extraction cells were fabricated for these studies. The small sampling devices constructed of 1/4 " tubing that were previously described also functioned as their own extraction cells. However, it was necessary to construct special high pressure cells to contain the authentic sampling devices for supercritical fluid extraction.

A schematic diagram of the extraction cell designed for the passive sampling device is shown in Figure 3. The cell was constructed entirely of 316 stainless steel (except for the O-ring) and was designed to avoid excessive dead volume. The body of the cell was a block with a cavity which provided a tight fit for the PSD. The cover plate was attached to the body with four bolts and sealed with a polymeric O-ring. This O-ring also sealed the PSD inside the the cell cavity so all fluid flow would go through the sampling device rather than around the edges. Two small discs with small channels milled on one side were placed on either side of the PSD and served to uniformly direct the fluid flow through the device. Small frits with 5 μm pores were also pressed into the inlet and outlet ports of the cell to prevent particle entrainment in the fluid. Appropriate Swagelok® fittings were connected to the cell to allow 1/16" o.d. tubing connections. The cartridge heater and temperature sensor were directly inserted into the body of the cell in appropriately sized holes. The cell was insulated by wrapping in glass fiber cloth.

A schematic diagram of the extraction cell designed for the VOST sampling tubes is shown in Figure 4. This cell was also constructed entirely of 316 stainless steel (except for polymeric

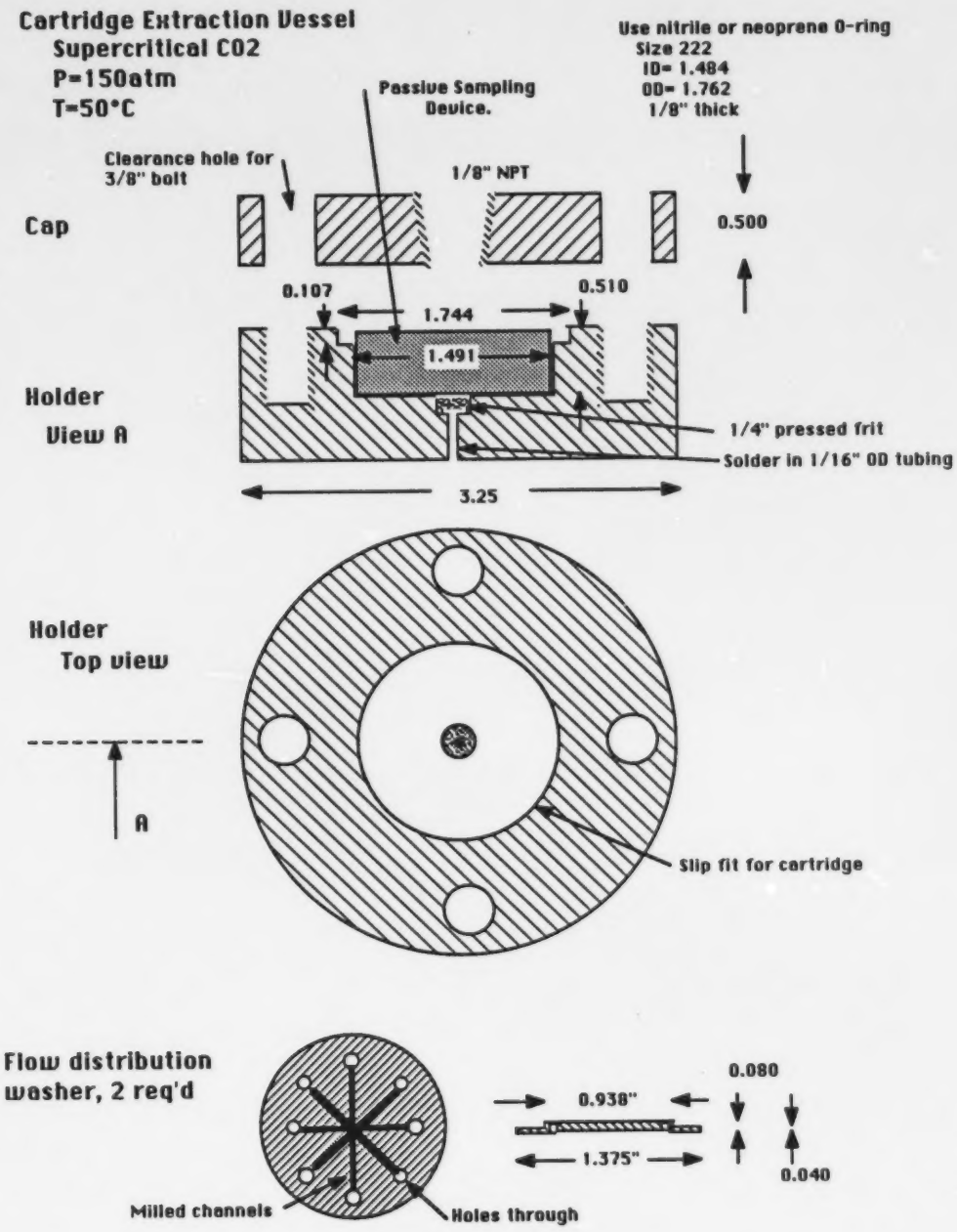

Figure 3. Schematic diagram of the passive sampling device extraction cell.

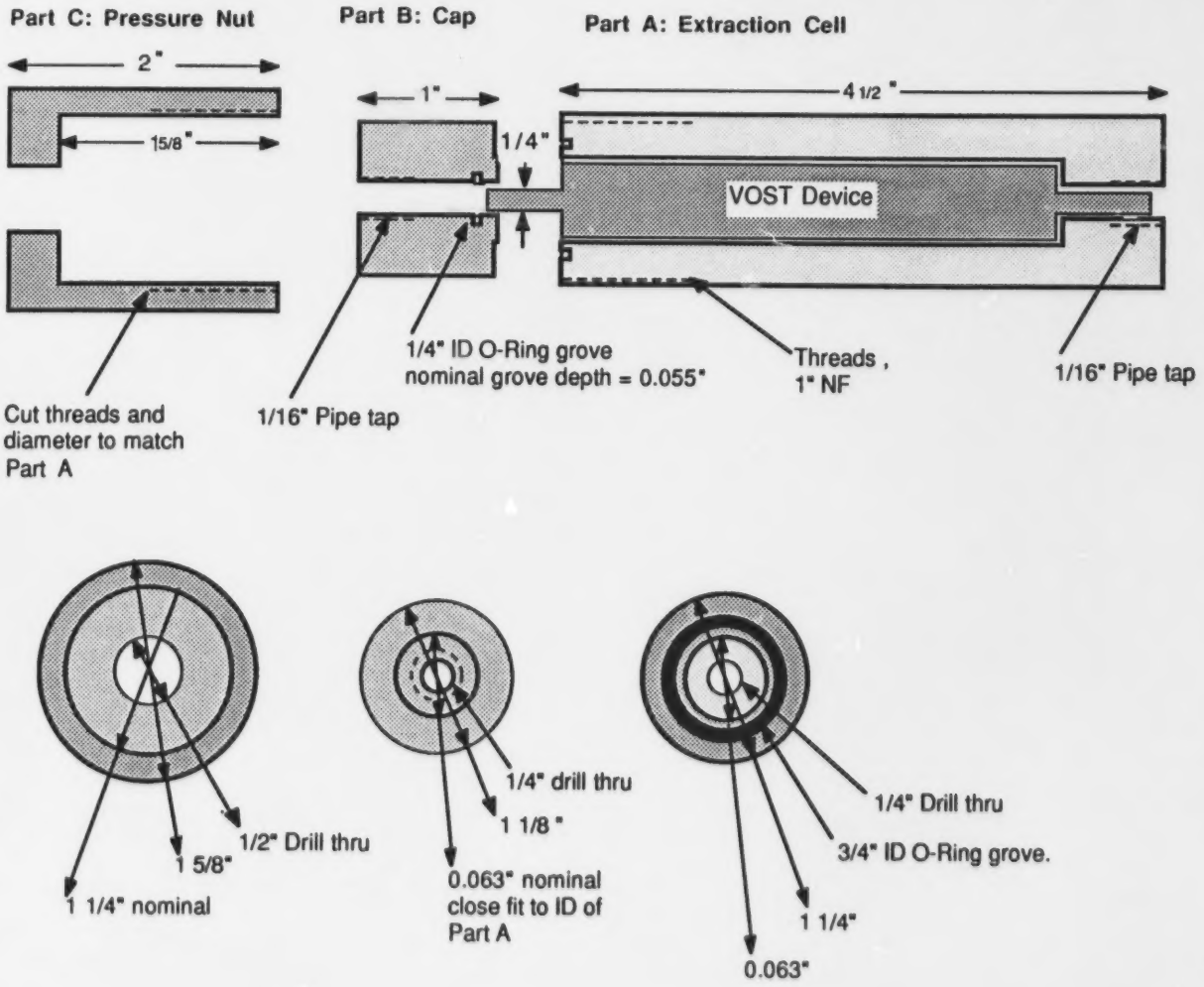

Figure 4. Schematic diagram of the VOST sampling tube extraction cell.

O-rings) and designed to avoid any excessive dead volume. Unfortunately, the VOST tubes were not uniformly sized and larger size tolerances were necessary which created unavoidable dead volume. The extraction cell consisted of a hollow tube in which the VOST device could be inserted. The cell was sealed with a cap and a polymeric O-ring held in place with a pressure nut. The 1/4" o.d. glass inlet end of the VOST tube was also sealed inside the body of the extraction cell with an additional O-ring to direct fluid flow through the device and prevent any flow around it. Connections to the cell were made by sealing short lengths of 1/8" o.d. x 0.020" i.d. s.s. tubing through appropriate Swagelok® fittings. The inside ends of these tubes were drilled out to accomodate 10 μm pore press-in frits and the outside ends were connected to the 1/16" transfer lines. The cartridge heater and temperature sensor were molded in aluminum foil which was wrapped around the cell body. The entire cell was then wrapped with insulating glass fiber cloth.

EXTRACTION-ANALYSIS PROCEDURES

Various extraction and gas chromatographic parameters were employed during the course of this investigation. Except for the exposure chamber spiked sampling devices, all other sampling devices were cleaned and conditioned by supercritical carbon dioxide extraction at 125 bar and temperatures ranging between 50° and 75°C for various lengths of time. After a device and its extraction cell provided a clean blank analysis (usually obtained after an iterative evaluation), the sampling device was spiked with standard VOC compounds and analyzed. Extraction times ranging from ten to thirty minutes were employed for both instrumentation designs. The carbon dioxide flow rate was sufficiently high in the final design that a somewhat elevated pressure was generated in the chromatographic retention gap. To prevent back flow of the extraction effluent into the carrier gas pneumatics the carrier gas inlet line was valved off during the extraction and for approximately 1-2 minutes after the extraction effluent was stopped. The chromatographic oven was held at -50°C during the extraction to aid solute focussing. After the extraction was completed and the carrier gas flow was resumed, the oven temperature was ramped at 15°C/min to 20°C, at 4°C/min to 110°C, and then at 10°C/min to the final temperature of 200°C. Since the high carbon dioxide flow extinquished the flame on the detector, the detector was re-ignited early in the temperature ramp.

Quantitative Analysis

Quantitative analysis was achieved by multi-level external calibration of the gas chromatograph. Response factors were determined for each VOC over the concentration range of interest. Standard gas mixtures were analyzed by connecting the retention gap inlet to a zero-volume fitting, six-port gas sampling valve fitted with an external sample loop. The sample

valve and loop were mounted inside a small enclosure that was heated to either 40°, 50° or 65°C. A constant temperature was used for each individual calibration sequence. Sample loops of 100, 250, 500 and 1000 µl volumes were used to inject various quantities of VOC. Due to suspected sorption losses of the VOC in various valves, three different valves were utilized. They included a used Valco "P" valve, a new Valco "P" valve, and a new Valco "T" valve. The "P" valves were rated for operation at temperatures up to 175°C and utilized ceramic filled Teflon® as a seal material. The "T" valve was rated for 300°C operation and used polyamide as the seal material. The sample loop was equipped with a septum inlet and a controlled back pressure outlet. Injections were made by purging and filling the sample loop to ambient pressure with various gas mixtures of known concentration using an all-glass syringe. Similar gas chromatographic analysis conditions as used for actual extraction-analyses were utilized. The detector signal was acquired and processed with a Nelson Analytical 4416 chromatographic data system. The initial calibration using the used "P" valve was obtained immediately prior to the actual analyses of the spiked adsorbent devices. During the quantitative portion of this investigation (6-8 weeks), the calibration was periodically checked and found to be stable. Calibrations using the new "P" and "T" valves were obtained several months after the actual analyses were made. However, since the gas flows to the detector were unchanged during this interval, the detector response would not be expected to have drifted more than 5-10%.

SECTION 5

RESULTS AND DISCUSSION

INSTRUMENTATION AND METHODOLOGY DEVELOPMENT

Preliminary Evaluations

The initial evaluation of on-line supercritical fluid extraction-gas chromatography for the analysis of VOC from adsorbent sampling devices involved two major concepts. They were: (1) Could a clean background be obtained by supercritical fluid extraction of an adsorbent device? and (2) Could the VOC's be extracted from the adsorbent matrix? Consequently, the early studies using the initial instrumentation design were aimed at answering these questions. The small sampling devices constructed of 1/4" stainless steel tubing filled with either Tenax® or Spherocarb® were used for these evaluations. After thermal conditioning of the devices, they were subjected to SFE-GC with carbon dioxide at 125 bar and 50°C. The Tenax® devices cleaned up after two or three supercritical fluid extraction cycles and gas chromatographic analyses could be obtained devoid of contaminants. However, even after numerous extraction cycles and extensive extraction periods (e.g., overnight), high levels of contamination were still present in extraction-gas chromatographic analyses of the Spherocarb® devices. It appeared as if some portion of the Spherocarb® matrix itself was soluble in supercritical carbon dioxide. Since the contaminants eluted in the same region as the VOC and were at such high concentration levels, the use of Spherocarb® was discontinued for the remainder of the studies.

To evaluate the second concept, clean Tenax® devices were spiked with methylene chloride and benzene vapors and subjected to SFE-GC analysis. The devices were crudely spiked by aspirating small volumes of air from above open bottles of these compounds through the devices. A typical chromatogram obtained from an SFE-GC analysis is shown in Figure 5. The Tenax® sampling device was extracted for two minutes (125 bar and 50°C) and the effluent collected at 0°C. After the extraction was completed, the gas chromatograph was temperature programmed at 8°C/min. Subsequent analyses of the same device yielded similar chromatographic profiles, but with decreasing peak intensity. Thus, it was clear that the volatile analytes were removed from the adsorbent by supercritical fluid extraction, but that complete extraction was not obtained in a single analysis. This could possibly be accounted for by the very high levels at which the

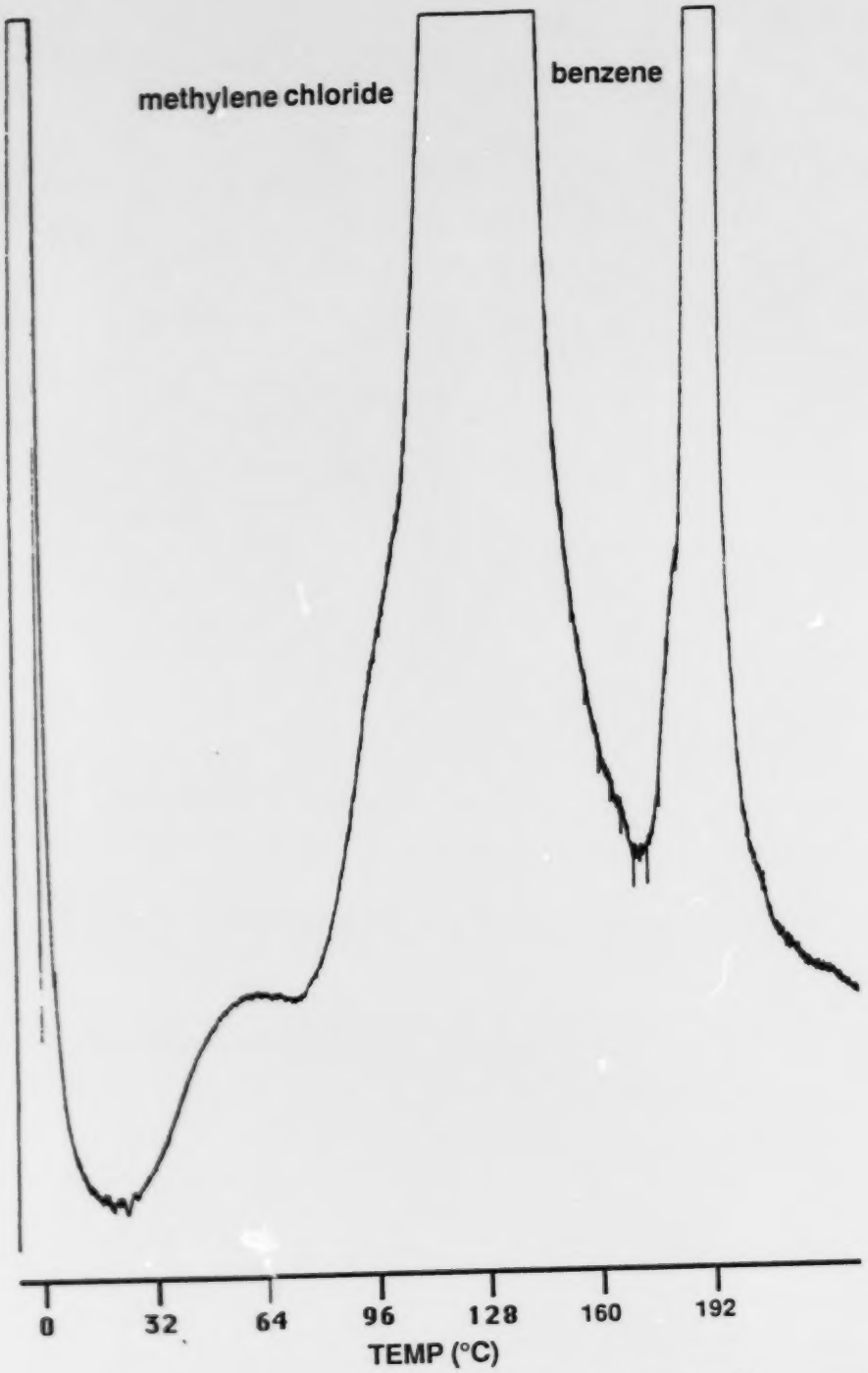

Figure 5. Chromatogram obtained from the SFE-GC analysis of a Tenax® sampling device.

devices were apparently being spiked. Efforts at spiking the devices at lower concentration levels were not successful, since either very high analyte levels or no detectable levels were always obtained. In addition to verifying that the spiking method was unacceptable, this behavior more importantly suggested that either an insufficient volume of extraction fluid was being used to remove low levels of analytes from the devices or that the analytes were not being efficiently trapped and recovered in the chromatographic column.

To test the latter possibility, the gas chromatography methodology was evaluated by directly connecting the inlet of the retention gap to a gas sampling valve and analyzing standard VOC mixture injections. Gas chromatographic methods for VOC analysis usually employ some form of "cold-trapping" to focus the analytes on the chromatographic column. The whole column cryotrapping method (9,10) was adopted for this study due to its simplicity (oven is cooled) and self diagnostic potential (e.g., if sharp peaks are obtained then the trapping was likely quantitative). The temperature at which whole column cryotrapping must be done for quantitative recoveries can be increased by using thick-film stationary phase columns. A recent study (10) has shown that efficient trapping of VOC can be obtained with a 3.0 μm stationary phase film column and a collection temperature of -20°C. Since a 5.0 μm stationary phase film column was used in this investigation, it was expected that a somewhat warmer collection temperature would prove adequate. However, as can be observed from the chromatograms shown in Figure 6, progressive improvements in chromatographic peak shape were obtained when cooler trapping temperatures were utilized. The chromatogram at the right was obtained with a trapping temperature of 30°C, the middle chromatogram with a trapping temperature of 0°C, and the chromatogram at the left with a trapping temperature of -20°C. No observable improvements in resolution or peak shape were obtained when cooler trapping temperatures were used. The chromatograms were obtained using a 0.32 mm i.d. column and approximately 50 ng/component injections. The magnitude of the signal response was reasonable for the amount of material injected at both the 0° and -20°C trapping temperatures which further substantiated that quantitative trapping was achieved.

As a final evaluation of the preliminary methodology, an exposure chamber spiked PSD with an accurately known loading of VOC's was subjected to analysis. Prior to analysis of the PSD, blank analyses of the empty extraction cell were made. Since the volume of the extraction cell and PSD was substantially larger than the small sampling devices, longer extraction times were utilized. The first blank analysis (20 minute extraction) yielded some moderate level contamination through the VOC region (up to 110°C) of the chromatgram. As might be anticipated, the next blank analysis was substantially cleaner with the VOC region free of contaminants. Unfortunately, a ten minute extraction and subsequent analysis of the PSD also

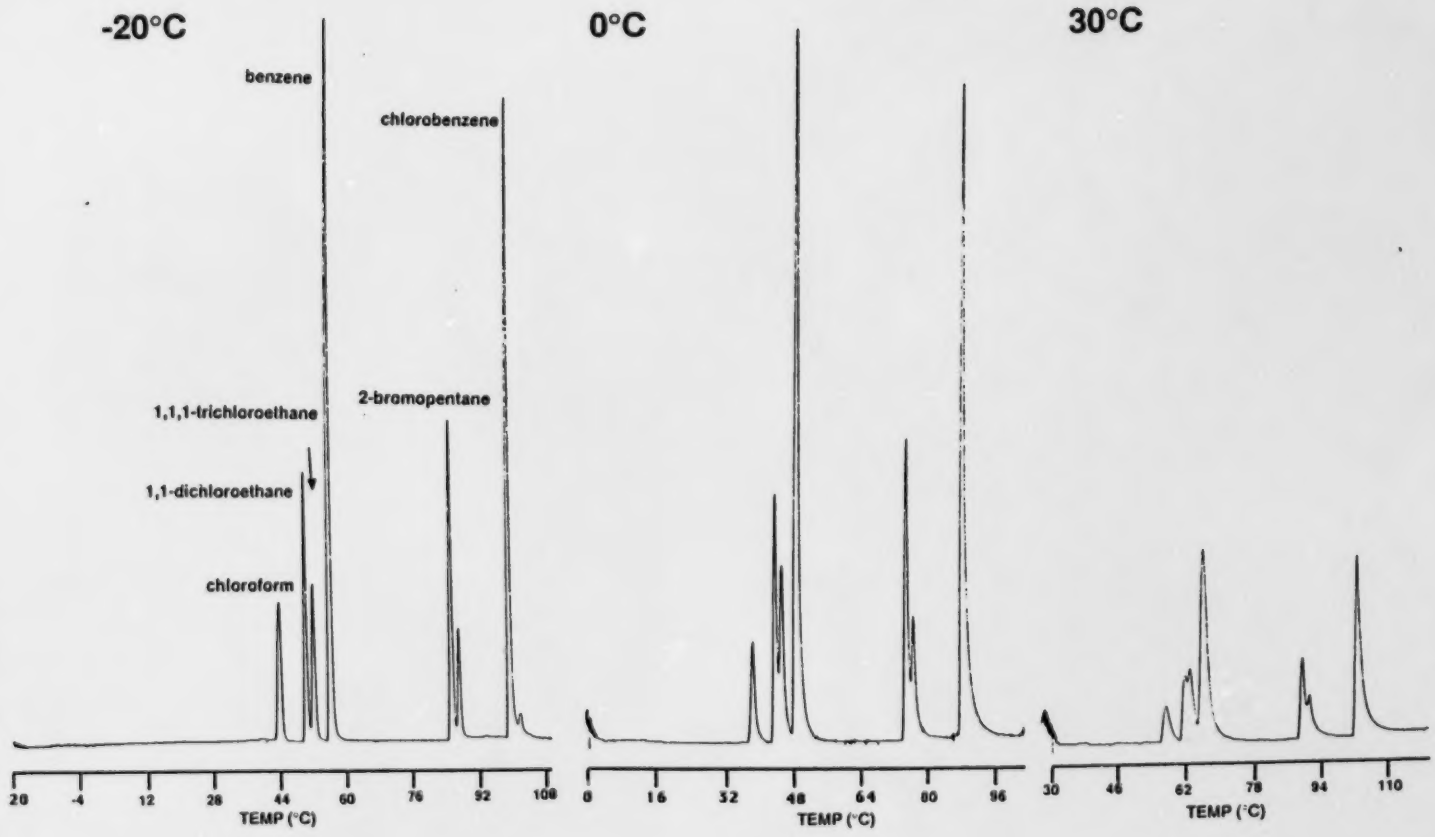

Figure 6. Chromatograms of a standard VOC mixture obtained at different whole column cryotrapping temperatures.

yielded a perfectly flat baseline, indicating that less than sub-nanogram quantities of the VOC were extracted from the PSD. The same device was subjected to a longer twenty minute extraction and essentially the same results were obtained, although a slight rise in the chromatographic baseline could be observed at the appropriate retention time. Even after spiking the PSD with up to 500 ng of a component, no discernible material could be detected after extractions of up to twenty minutes. Consequently, it was concluded that much larger extraction fluid volumes would be necessary to quantitatively extract realistic VOC loadings. This was not unexpected since a twenty minute extraction time would have only used ~200 µl of fluid.

Instrumentation Modifications

To obtain higher extraction fluid flow rates it was necessary to modify the instrumentation. The basic concept of the on-line extraction-analysis approach required the extraction effluent to be passed through the chromatographic column. The standard 0.32 mm i.d. capillary column could only tolerate approximately 10 mL/min of gas flow from the extraction effluent before pressure would build up and backflush extraction effluent into the carrier gas pneumatics. Two approaches were taken to overcome this problem. First, a larger diameter capillary column was substituted for the smaller diameter column and the carrier gas inlet was valved so it could be isolated from the chromatographic column during extraction. By utilizing a 0.53 mm i.d. capillary column (megabore), high separation efficiencies could be maintained to resolve the closely eluting VOC, yet more than three times greater gas flow from the extraction effluent could be tolerated without excessive pressure build-up. Furthermore, by isolating the carrier gas from the chromatographic column during the extraction, a nominal increase in pressure would not create any serious problems. The pressure would dissipate shortly after the extraction was completed and the carrier gas flow could be resumed.

These modifications were made and the depressurization restrictor was modified to allow approximately a 100 mL/min gas flow (100 µl/min fluid flow). Although the detector flame was extinquished, this higher flow rate did not present any problems as long as ambient or warmer conditions were maintained. However, as soon as the oven was cooled to temperatures lower than 0°C to trap the volatile analytes, the fused silica column (retention gap) would freeze closed near the end of the restrictor and completely stop the extraction effluent flow. This problem was overcome by building a separate expansion region from a short length of glass-lined stainless steel tubing (0.020" i.d.) that was clamped in a heated metal block. The higher heat capacity and better heat transfer properties of the glass-lined stainless steel (compared to fused silica) allowed sufficient heat to be transferred to the expansion region to prevent the carbon dioxide extraction effluent from freezing (11). A 2 m x 0.53 mm i.d. fused silica retention gap was connected between the expansion tube and the analytical column to facilitate trapping of the volatile analytes.

The modified instrumentation was evaluated using a small sampling device spiked with approximately 250 ng of each of the standard VOC compounds. A chromatogram of this extraction-analysis is shown in Figure 7. The device was extracted for ten minutes with carbon dioxide at 125 bar and 50°C. The oven was cooled to -20°C during the extraction to trap the volatile analytes. After the extraction was completed the oven temperature was programmed from -20° to 40°C at 10°C/min and then at 4°C/min. Several poorly shaped peaks appeared in the chromatogram at retention times corresponding to the standard VOC compounds. Retention time windows for the standard VOC compounds had been previously determined from valve injections of the standard VOC mixture. Since a clean blank extraction-analysis was obtained from the sampling device before it was spiked with standard VOC compounds, it was concluded that the larger extraction fluid volume (~1 mL) successfully extracted the standard VOC compounds. However, judging from the poor chromatographic peak shape and the lower intensity of the more volatile compounds, it was obvious that inadequate trapping measures were being taken. As might be anticipated, the higher flow conditions from the extraction presented more challenging analyte trapping conditions (compared to valve injections). To determine if additional material could be recovered, the device was subjected to a second identical extraction-analysis. The chromatogram was essentially clean except for a similar contaminant peak eluting immediately after benzene. These results suggested that the standard VOC compounds were probably quantitatively removed in the first extraction, but not quantitatively recovered and analyzed.

To obtain more efficient trapping of the analytes, a cooler whole-column cryotrapping temperature of -50°C was utilized. This was the coldest practical temperature achievable since carbon dioxide freezes at approximately -57°C (at 1 bar). A chromatogram obtained from the extraction-analysis of a sampling device spiked with approximately 175 ng of each standard VOC compound using the cooler collection temperature is shown in Figure 8. Again, a relatively clean blank analysis was obtained prior to spiking the device. The extraction was conducted for fifteen minutes at a higher carbon dioxide temperature of 75°C. Although the fluid density was significantly lower at the higher temperature and constant pressure of 125 bar (0.35 vs. 0.62 g/mL), higher solubility of the volatile analytes in the fluid would be expected at the higher temperature. After the extraction was completed, the oven temperature was ramped from -50° to 20°C at 15°C/min and then at 4°C/min to the maximum temperature. The cooler trapping temperature significantly improved the chromatographic peak shapes and increased the signal intensity for the standard VOC compounds (inspite of lower quantities being spiked on the device). In addition, several other contaminant peaks were present in the chromatogram which could presumably be attributed to impurities in the carbon dioxide. These peaks were particularly

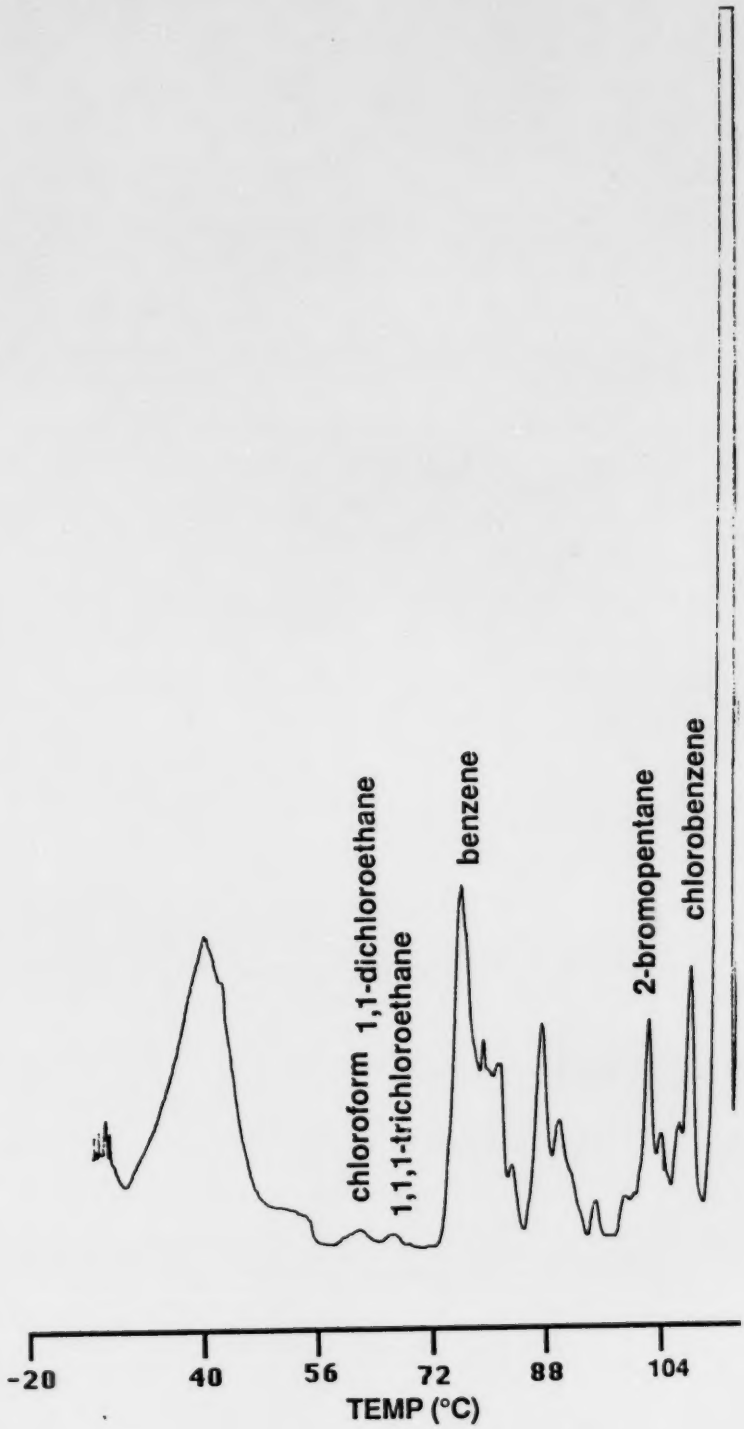

Figure 7. SFE-GC chromatogram of a spiked sampling device obtained using a 100 mL/min gas extraction flow rate and a -20°C trapping temperature.

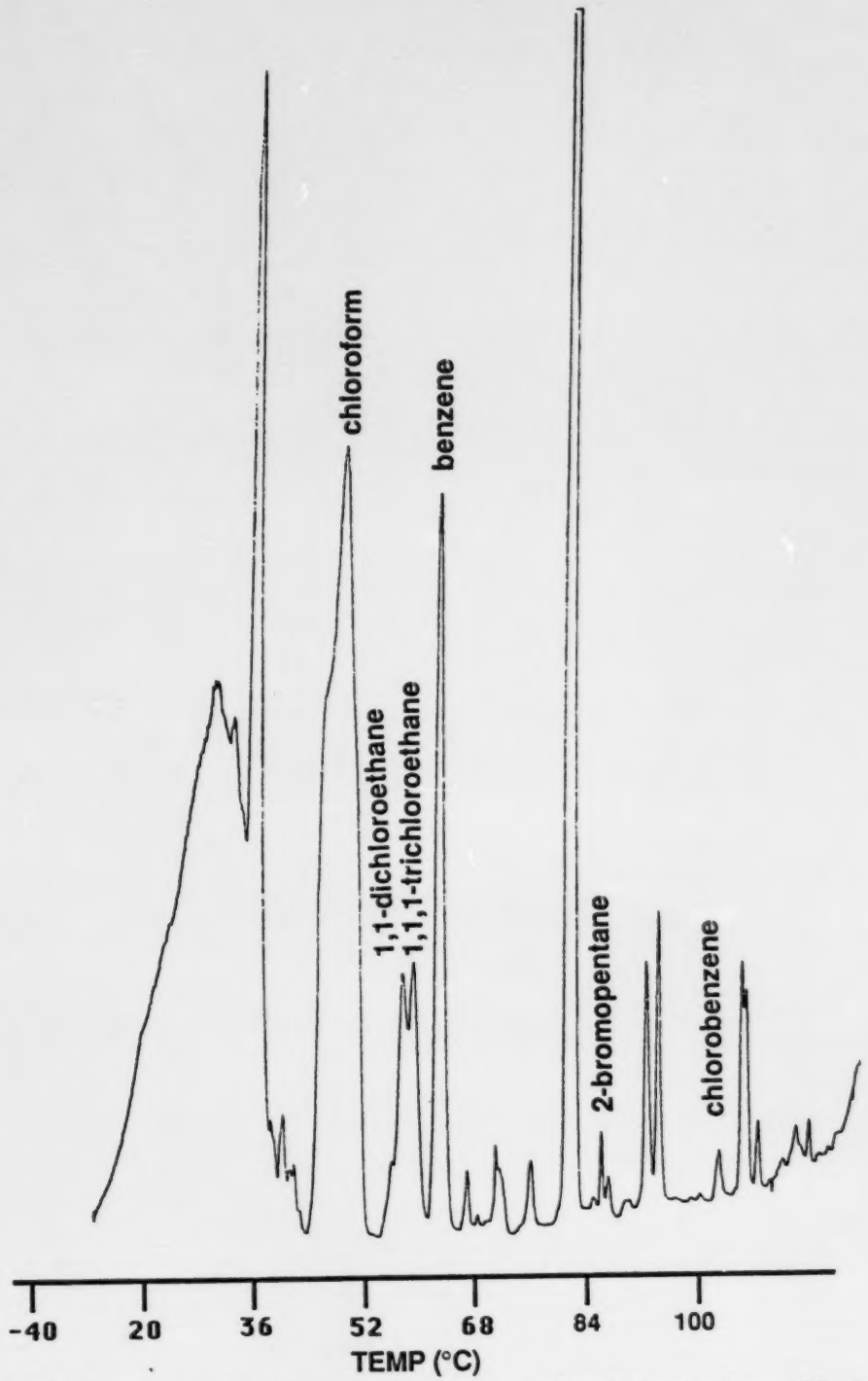

Figure 8. SFE-GC chromatogram of a spiked sampling device obtained using a 100 mL/min gas extraction flow rate and a -50°C trapping temperature.

noticeable when a second extraction-analysis was performed on the same sampling device to determine if any additional standard VOC compounds could be extracted. A large contaminant eluting over the retention window of chloroform was verified, but no perceptible levels of the other standard VOC compounds were detected. Unfortunately, as larger fluid volumes and improved trapping procedures were developed, increased problems with fluid purity were encoutered.

Although improved chromatographic peak shapes and higher signal intensities were obtained by utilizing the cooler trapping temperature, further improvements in both peak shape and collection efficiency were needed. Consequently, a 15 m x 0.53 mm i.d. fused silica retention gap was substituted for the short two meter retention gap. A chromatogram from the extraction-analysis of a sampling device spiked with approximately 100 ng of each standard VOC compound is shown in Figure 9. Similar extraction and chromatographic parameters were used for this analysis as the one described in Figure 8, except that a 25 minute extraction period was utilized. The longer retention gap significantly improved the chromatographic peak shapes and the analyte collection efficency. Much larger signal intensities were obtained even if smaller quantities of the standard VOC compounds were spiked on this device. Qualitatively, the signal response appeared appropriate for the amount of material present on the device and the chromatographic peak shapes were reasonably sharp suggesting that quantitative trapping and collection had been obtained. The second extraction-analysis of the same device did not detect any material in the chromatographic retention windows for the standard VOC compounds which suggested that quantitative removal of the VOC occurred with the first extraction. High levels of contamination from impurities in the carbon dioxide were present in the early segment of the chromatographic analysis, but they did not overlap and interfere with the standard VOC compounds selected for these studies.

Extraction Fluid Purification

Another significant problem that had to be overcome was adequate purification of the carbon dioxide extraction fluid. Since large volumes of gaseous carbon dioxide (up to six liters) were passed through the chromatographic column and subjected to analyte trapping and concentration conditions, very low levels of trace impurities could create serious contamination problems. As improved extraction and collection methodologies were developed, these problems became more evident. This is illustrated with the example chromatogram shown in Figure 10. This analysis was obtained from a ten minute extraction using the same instrumental configuration as used for the analysis shown in Figure 9, except the extraction cell had been by-passed. Consequently, all of the chromatographic peaks could be attributed to impurities in the carbon dioxide. As can be observed, the level of contamination was quite substantial with several impurities eluting in the

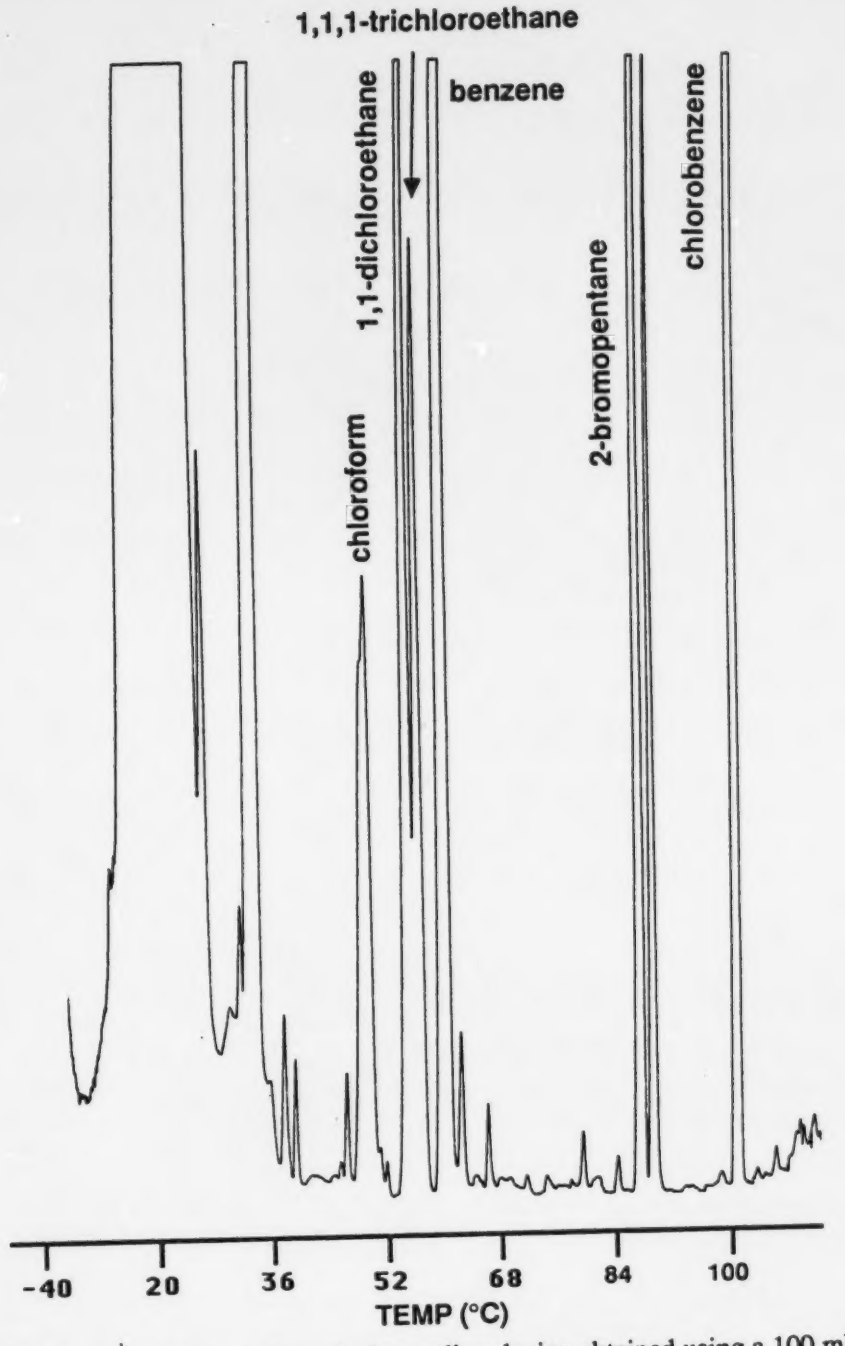

Figure 9. SFE-GC chromatogram of a spiked sampling device obtained using a 100 mL/min gas extraction flow rate, a -50°C trapping temperature, and a 15 m retention gap.

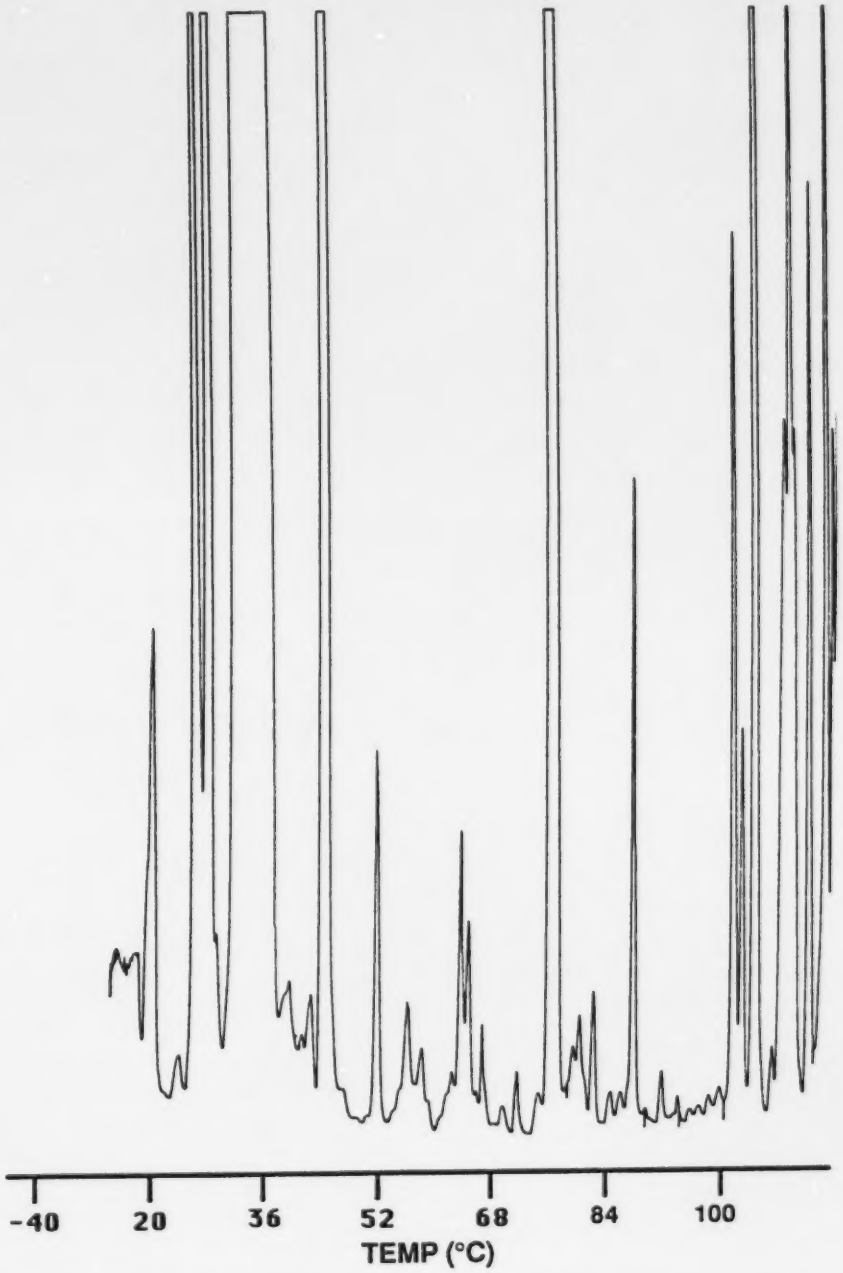

Figure 10. SFE-GC chromatogram obtained from a ten minute blank extraction showing the impurities in the carbon dioxide extraction fluid.

retention time windows of the standard VOC. This extraction utilized "high purity" carbon dioxide that had been further purified by flowing it through a bed of activated charcoal while the syringe pump was being filled (otherwise much greater contamination would have been observed).

The level of contamination in the chromatogram shown in Figure 10 can be contrasted to the much lower level observed in the chromatogram shown in Figure 9. The cleaner carbon dioxide used in the analysis described in Figure 9 was obtained by distilling the carbon dioxide gas from the cylinder, passing it through the activated charcoal trap, and recondensing it in the syringe pump. This procedure required using carbon dioxide from a cylinder without an eductor tube and cooling of the syringe pump head to ~ 0°C. By using activated charcoal that had been freshly baked at 250°C, the large contaminants eluting below 40°C in the chromatograms could also be eliminated. Chromatograms using such purified carbon dioxide are discussed later in the report. It was necessary to replace the activated charcoal frequently to maintain high purity fluid.

QUANTITATIVE VALIDATION STUDIES

In addition to the qualitative studies described in the previous section, all three sampling devices were subjected to quantitative extraction-analyses. The chromatographic system was calibrated by an external standard method and sampling devices that had been spiked with known quantities of standard VOC compounds were subsequently analyzed.

Instrument Calibration

Instrument calibration was accomplished by injecting known concentrations of the standard VOC compounds using a gas sampling valve. Three different valves were used to obtain independent calibrations since it was suspected that sorption losses of the VOC were occurring and distorting the calibration. A typical chromatogram of a VOC standard obtained with the used Valco "P" valve is shown in Figure 11. This chromatogram and all other analyses used for instrument calibration utilized the 15 m retention gap and the same oven temperature profile as used for extraction-analyses (e.g., -50°C collection temperature). The larger diameter capillary column provided excellent separation of the mixture components including base-line resolution of the 1,1-dichloroethane from the 1,1,1-trichloroethane and the two bromopentane isomers from each other. Presumably, the compound eluting immediately after 2-bromopentane is 1-bromopentane. In fact, the larger i.d. column provided better separations than the smaller i.d. column (see Figure 6).

The calibration plots for the standard VOC compounds obtained with the used "P" valve are shown in Figure 12. Calibration was obtained by fitting the signal response of three replicate

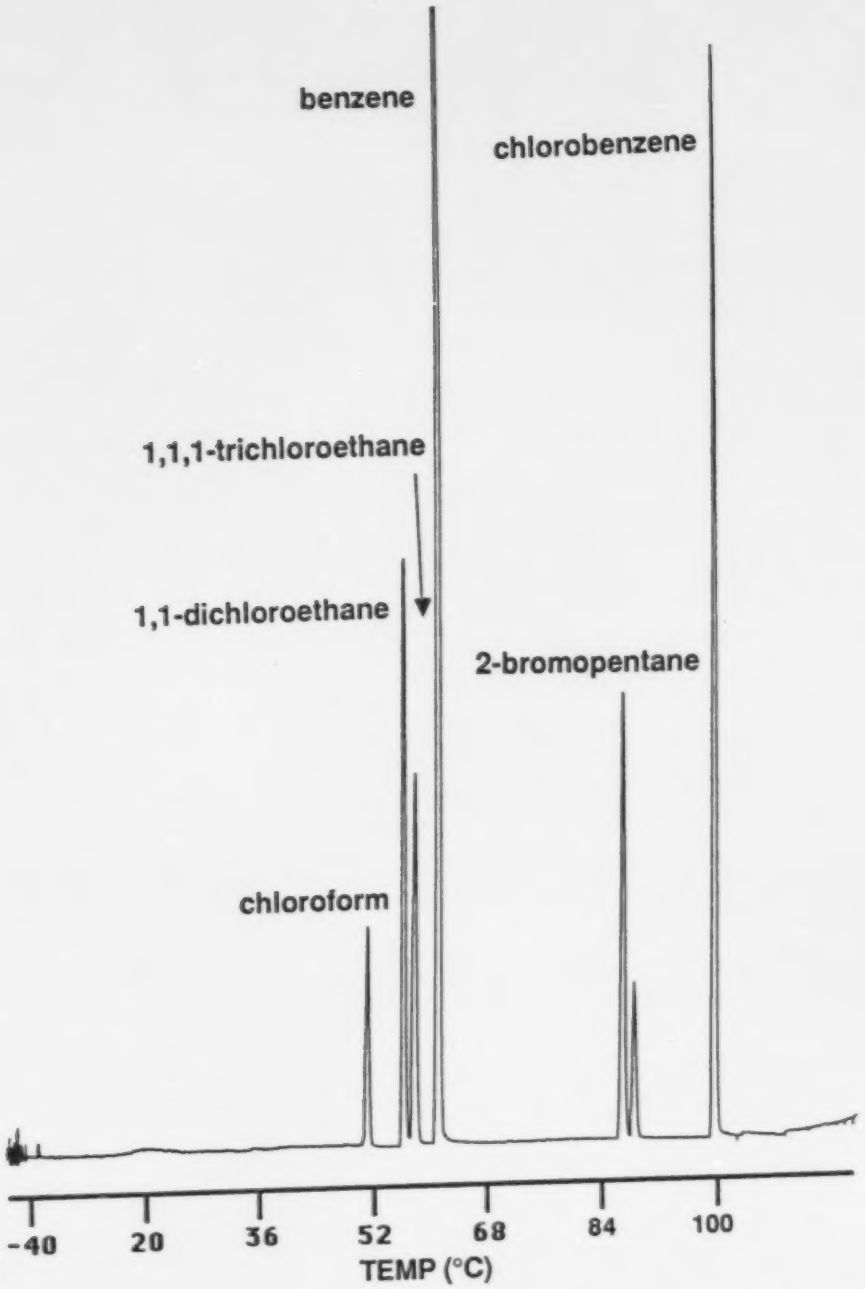

Figure 11. GC chromatogram of the VOC mixture obtained using a sampling valve injection.

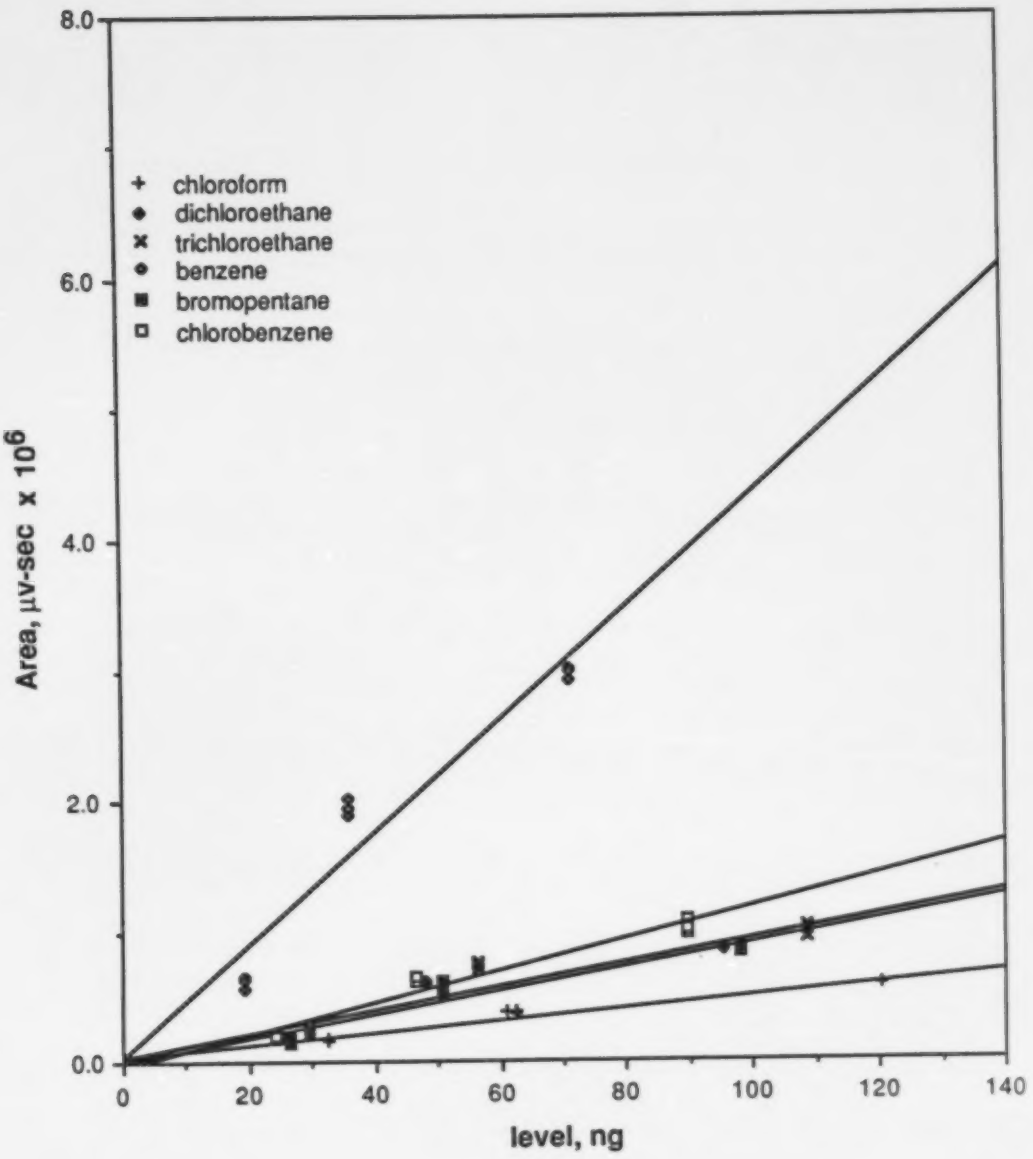

Figure 12. FID calibration plots of the standard VOC compounds obtained with the used "P" valve.

injections at three concentration levels for each analyte to a linear regression equation. Different standard mixtures were prepared to obtain different concentration injections. The valve and the 500 µl sample loop were heated to 40°C for this calibration. As expected, significant differences in FID response were obtained for the individual VOC compounds. Benzene gave the greatest response followed by significantly lower responses for chlorobenzene, bromopentane, dichloroethane, trichlorethane, and chloroform. The relative standard deviations for the replicate measurements ranged between 0.9 and 12% indicating that some difficulty in obtaining reproducible injections was experienced.

The coefficients for the linear regression equations defining the response of the standard VOC compounds and the standard error estimates for these coefficients are listed in Table 1. As can be observed from the calibration plots shown in Figure 12, the individual response values do not fall directly on the lines predicted by the regression equations. This lack of fit is characterized by the correlation coefficients (R) being somewhat less (0.93 to 0.98) than the desired 0.99 or 1.00. The uncertainty of the predicted values from the regression equations arising from this lack of fit is reflected in the relative standard errors of slope which range from 8 to 15%. Although some uncertainty could have resulted from errors in standard mixture preparation, analyte sorption losses could also contribute to nonlinear calibrations.

TABLE 1. DETECTOR CALIBRATION DATA FOR THE STANDARD VOC MIXTURE OBTAINED WITH THE USED "P" VALVE

Compound	Coefficients*		Standard Error Estimate		Correlation
	slope	intercept	slope	intercept	Coefficent (R)
Chloroform	4610	42276	354 (8%)†	28452	0.98
Dichloroethane	9042	41202	1253 (14%)†	79588	0.94
Trichloroethane	8772	85516	1323 (15%)†	95995	0.93
Benzene	43084	36925	4718 (11%)†	223216	0.96
Bromopentane	9018	1140	1059 (12%)†	69335	0.96
Chlorobenzene	12214	-33597	1087 (9%)†	65173	0.97

* for the linear equation $y = mx + b$, where y is the signal response and x is the analyte level in ng.

†Relative Standard Error

Utilization of the response factors in Table 1 gave excessively high recoveries (e.g., > 500%) for actual extraction-analyses, which provided further evidence for possible sorption losses of the VOC analytes in the injection valve and subsequent inaccurate calibration. Consequently, a second independent calibration was done using a new Valco "P" valve. For this calibration, a single VOC standard mixture was utilized with 100, 500, and 1000 µl sample loops to obtain different concentration injections. The valve and the respective sample loop were heated to 50°C. The calibration plots for the standard VOC compounds from this calibration are shown in Figure 13. The reproducibility of the replicate analyses was much bettter than the previous calibration with the relative standard deviations generally less than 3%. The coefficients for the linear regression equations defining the response of the VOC compounds and the standard error estimates for these coefficients for this calibration are listed in Table 2. The slopes and the ratios of the slopes of the regression equations for the various VOC are substantially different than those listed in Table 1. The correlation coefficients (R) were all 1.00 indicating good fit of the data by the equation. Furthermore, the standard error estimates on the slopes were low, further indicating good fit of the calibration points by the equation and low uncertainty in the predicted values from the calibration.

TABLE 2. DETECTOR CALIBRATION DATA FOR THE STANDARD VOC MIXTURE OBTAINED WITH THE NEW "P" VALVE

Compound	Coefficients*		Standard Error Estimate		Correlation Coefficent (R)
	slope	intercept	slope	intercept	
Chloroform	4723	7961	119 (2.5%)†	9149	1.00
Dichloroethane	12400	8180	235 (1.9%)†	14286	1.00
Trichloroethane	12410	22980	398 (3.2%)†	27558	1.00
Benzene	55450	40720	1525 (2.8%)†	68964	1.00
Bromopentane	22460	18270	807 (3.6%)†	50342	1.00
Chlorobenzene	33970	19040	1533 (4.5%)†	87548	1.00

* for the linear equation $y = mx + b$, where y is the signal response and x is the analyte level in ng.

†Relative Standard Error

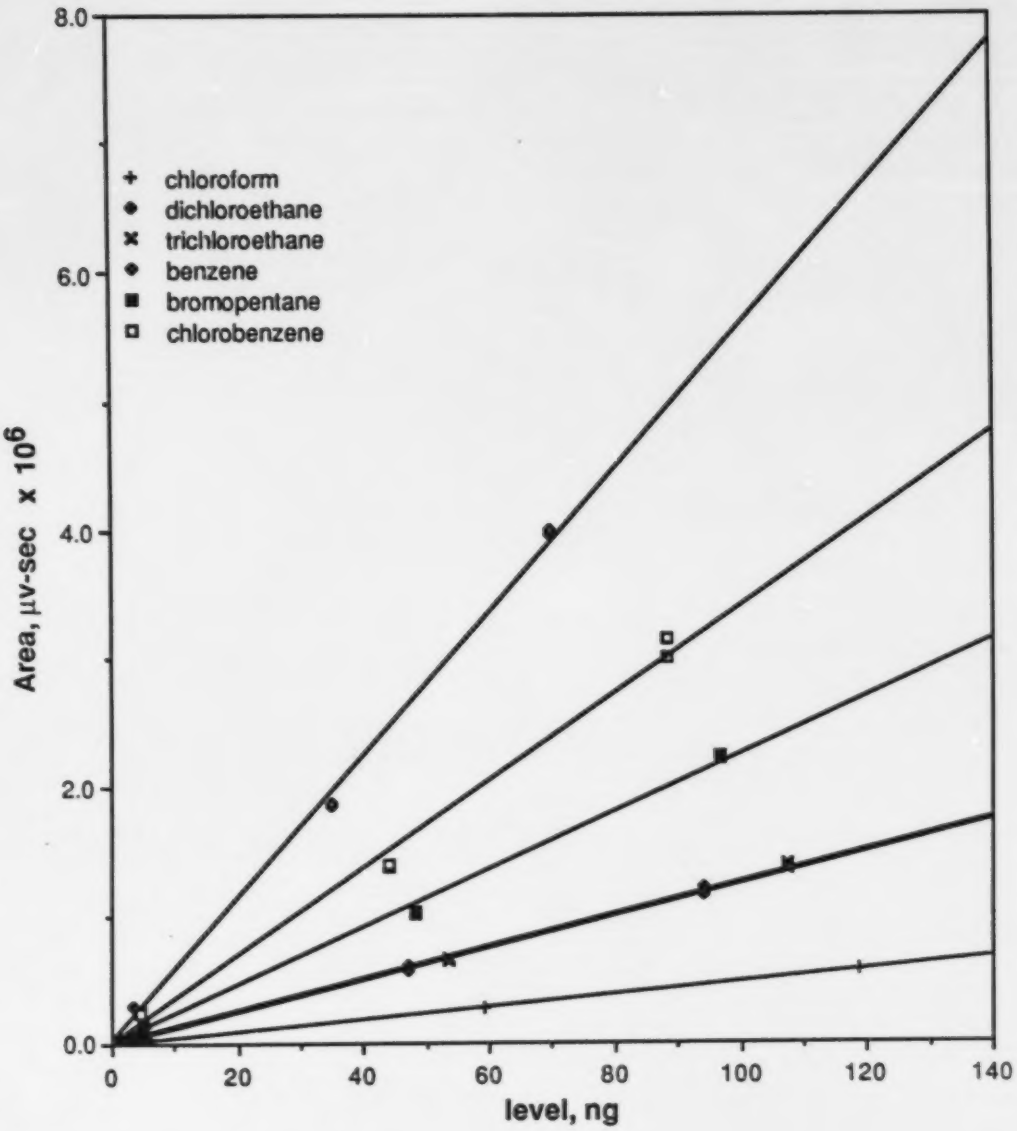

Figure 13. FID calibration plots of the standard VOC compounds obtained with the new "P" valve.

Although this calibration was statistically more precise, the calculated recoveries were still excessively high. On the assumption that there could be active sites in the injector, a more concentrated (10^3) VOC mixture was purged through the valve to (irreversibly) attach to and deactivate any active sites. After the valve had been adequately purged, the responses of the VOC were again determined and found to be approximately 20% greater. Small ghost peaks corresponding to all of the VOC and five additional peaks could be observed with blank injections following this treatment. The valve was again flushed with a concentrated VOC mixture and allowed to purge overnight. The performance of the valve was then evaluated and it was found that similar responses were obtained for chloroform, trichlorethane, and benzene, but that the responses of the dichloroethane, bromopentane, and chlorobenzene had decreased. Furthermore, it was not possible to obtain reproducible responses from replicate injections. This behavior suggested that the compounds were being selectively adsorbed by the polymeric seal material (ceramic filled Teflon®) in the valve. This was somewhat unexpected since Teflon® materials have been used extensively in VOC analytical methods.

A third calibration was then obtained using a Valco "T" valve which uses polyamide as the seal material. As an extra precaution injections were made with an all-glass syringe. Four sample loops with volumes of 100, 250, 500, and 1000 µl were used to obtain different injection concentrations. The valve and the respective loop were heated to 65°C. The calibration plots for the VOC from this calibration are shown in Figure 14. Reproducible responses were obtained between replicate injections with the relative standard deviations generally being less than 3%. The coefficients for the linear regression equations defining the response of the VOC compounds and the standard error estimates for these coefficients for this calibration are listed in Table 3. Again, the slopes and the ratios of the slopes of the regression equations for the various VOC are significantly different than those obtained in the previous calibrations described in Tables 1 and 2. Infact, the response for benzene, the compound from the standard mixture that would be expected to be least susceptible to adsorption by Teflon®, increased by a factor of 1.3 from the first to second calibration and by 1.7 from the second to third calibration. The linear regression equations fit the calibration points very well as reflected by correlation coefficients (R) of 1.00. The expected uncertainty of predicted values from the calibration was corresponding low with the relative standard error on the regression slopes generally being less than 2%. This calibration was used to calculate the quantitative recoveries for the studies described in this report.

Preliminary Sampling Device

The small sampling devices used for instrumentation and methodology development were also subjected to quantitative analysis. However, as a final modification of the methodology, the depressurization restrictor was shortened to increase the extraction gas flow rate to approximately

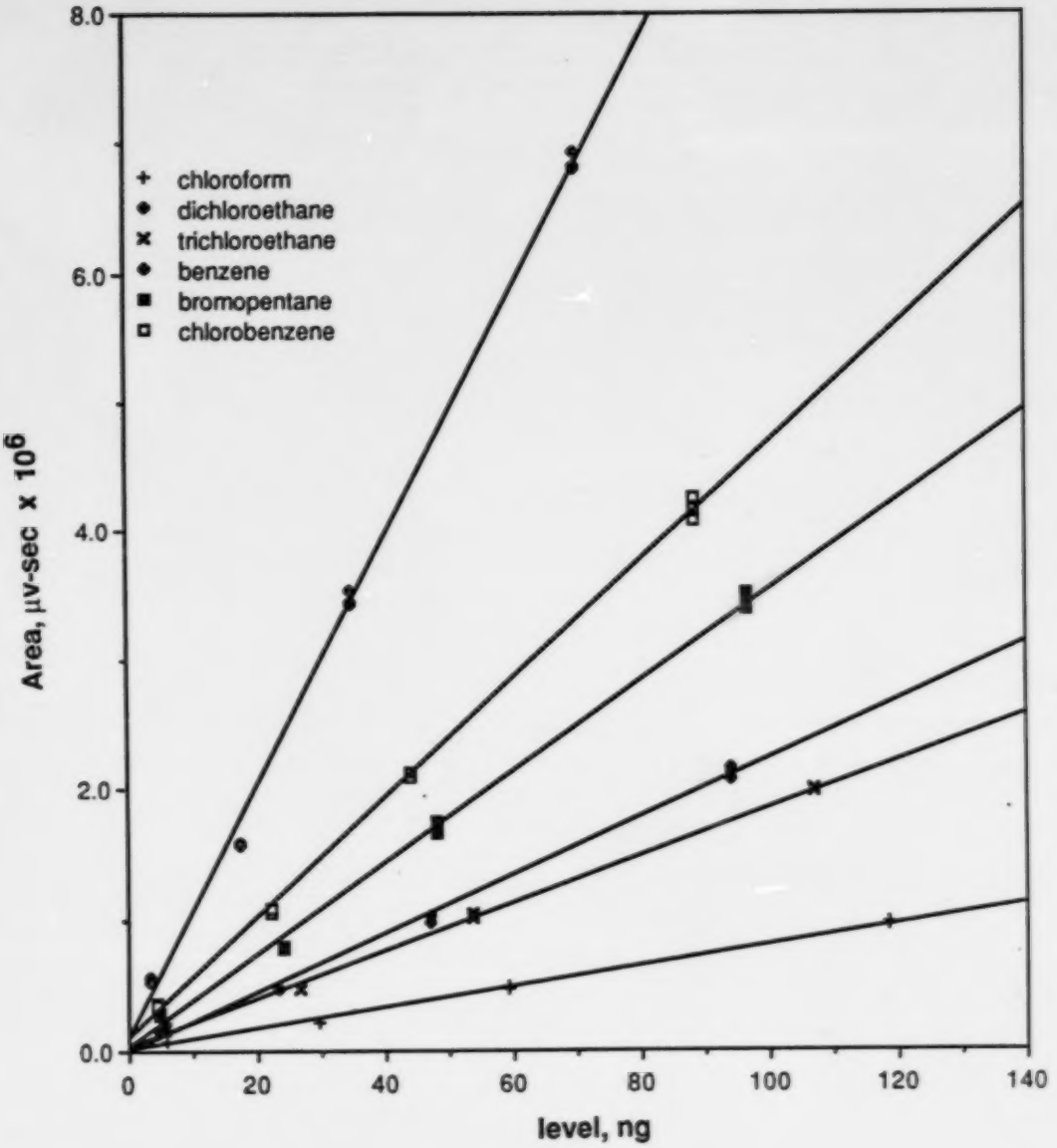

Figure 14. FID calibration plots of the standard VOC compounds obtained with the new "T" valve.

TABLE 3. DETECTOR CALIBRATION DATA FOR THE STANDARD VOC MIXTURE OBTAINED WITH THE NEW "T" VALVE

Compound	Coefficients* slope	intercept	Standard Error Estimate slope	intercept	Correlation Coefficent (R)
Chloroform	7930	14760	128 (1.6%)†	8996	1.00
Dichloroethane	22450	-3617	455 (2.0%)†	25417	1.00
Trichloroethane	18160	44960	282 (1.6%)†	17944	1.00
Benzene	96170	102500	1464 (1.5%)†	60874	1.00
Bromopentane	35070	42950	640 (1.8%)†	36741	1.00
Chlorobenzene	45810	111200	549 (1.2%)†	28854	1.00

* for the linear equation $y = mx + b$, where y is the signal response and x is the analyte level in ng.

†Relative Standard Error

200 mL/min (factor of two) to provide a corresponding increase in the extraction speed. The more rapid flow rate did not seem to adversely affect focusing of the VOC analytes, but greater total flow volumes tended to proportionally increase chromatographic band broadening of the analytes. In other words, the chromatographic peaks were as sharp for a ten minute extraction at 200 mL/min gas flow as a twenty minute extraction at 100 mL/min, but a twenty minute extraction at 200 mL/min displayed wider and less efficient peaks. This behavior suggested that it was not only the rapid flow rate that was creating a difficult trapping and collection environment, but the large gas volume that was being passed through the column.

For the quantitative studies, more realistic loading levels on the order of 60 ng of each component were spiked on the devices. Typical chromatograms from an analysis sequence are shown in Figures 15-17. The chromatogram from the blank extraction-analysis of the sampling device prior to spiking is shown in Figure 15. Several prominent contaminants from the ten minute carbon dioxide extraction were present early in the chromatogram, but at temperatures above 45°C, the analysis was relatively clean. The chromatogram from the actual extraction-analysis of the device after it was spiked is shown in Figure 16. This extraction was conducted for ten minutes with the fluid at 125 bar and 75°C. Again, the contaminants from the carbon

Figure 15. SFE-GC chromatogram of a blank analysis of a sampling device prior to spiking with the standard VOC.

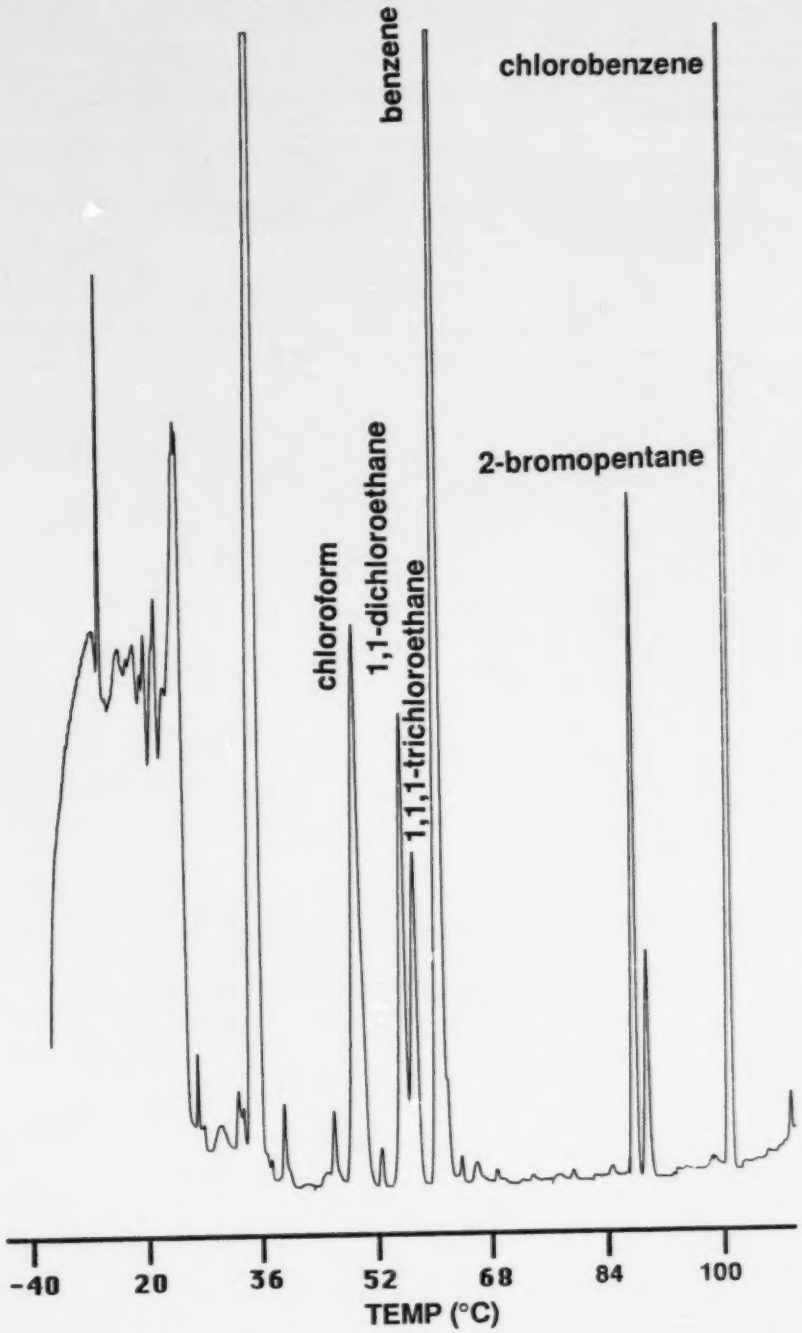

Figure 16. SFE-GC chromatogram from the analysis of a spiked sampling device.

Figure 17. SFE-GC chromatogram from the second analysis of the sampling device from Figure 16.

dioxide were present early in the chromatogram, but did not interfere with the standard VOC compounds that eluted in their expected retention time windows. A second ten minute extraction-analysis of the same device was also conducted to determine if additional quantities of the standard VOC compounds could be recovered. This chromatogram is shown in Figure 17 and as can be observed, no additional quantities of VOC were detected which provided strong evidence that the analytes had been quantitatively extracted.

The actual loading levels and recovered quantities of each of the VOC standard compounds from this analysis (Run 3) and two other similar analyses are listed in Table 4. With the exception of chloroform, the recovered levels of standard compounds exhibited fairly close agreement to the loading levels. Recoveries ranged from 71 % to 171 % with most of the recoveries falling within a 15 % margin of the loading level. An obvious contaminant (partially resolved overlapping peak, but integrated as a single peak) eluted with the chloroform peak in Run 2, and it is possible that a similar contaminant was also present in Run 1 and 3 which could account for the excessively high recoveries of chloroform. It is possible that contamination could have occurred during the spiking procedure.

TABLE 4. RECOVERY DATA FROM PRELIMINARY SAMPLING DEVICES

Compound	Run 1		Run 2		Run 3	
	Loading Level (ng)	Recovered Amount (ng)	Loading Level (ng)	Recovered Amount (ng)	Loading Level (ng)	Recovered Amount (ng)
Chloroform	64	291 ± 6	77	567 ± 10*	77	327 ± 6
Dichloroethane	50	59 ± 2	61	74 ± 3	61	66 ± 3
Trichloroethane	56	42 ± 2	70	50 ± 2	70	59 ± 2
Benzene	38	36 ± 1	46	42 ± 15	46	45 ± 1
Bromopentane	52	50 ± 2	63	51 ± 2	63	55 ± 2
Chlorobenzene	47	80 ± 2	57	61 ± 1	57	57 ± 1

*Included obvious overlapping contaminant

The listed errors (usually less than 5 %) for the calculated recovery values only reflect the uncertainty associated with the calibration. These values were obtained by appropriate modification of the linear regression equations with the standard error estimates on the slopes and intercepts. Uncertainty associated with the standard mixture preparation and adsorbent spiking, and drift in the calibration could possibly contribute an additional 10 to 15% of error.

Authentic Passive Sampling Devices

The EPA passive sampling device was subjected to similar studies in which a clean device was spiked with standard VOC compounds and analyzed. A chromatogram of an extraction-analysis of this type of device is shown in Figure 18. The extraction was conducted for twenty minutes using carbon dioxide at 125 bar and 65°C. The lower temperature (compared to 75°C for the preliminary devices) was used to minimize potential contamination from the polymeric O-ring sealing the extraction cell. Although the device was presumably spiked with approximately the same quantites of standard VOC compounds as the preliminary devices described in the previous section, much larger chromatographic peaks were obtained. Fortunately, this can be accounted for since it was determined that the syringe used to spike the device was contaminated with higher levels of the standard VOC compounds (e.g., the syringe had not been cleaned after making the serial dilution during preparation of the standard mixture). A second fifteen minute extraction-analysis of the same device was also conducted to determine if additional quantities of standard VOC compounds could be recovered. This chromatogram is shown in Figure 19, and as can be observed, only very small peaks corresponding to the chloroform and benzene elution times were detected. The larger peak corresponding to the elution time of benzene may contain two components, both of which are probably contaminants. These results indicated that very high levels (>400 ng benzene) of the standard VOC compounds could be successfully solvated and extracted from the PSD with the volume of extraction fluid utilized (~ 4 mL) in the current methodology. The carbon dioxide used in these extractions was much cleaner than used for the extractions described in the previous section as evidenced by the clean baselines in the early portions of the chromatograms shown in Figures 18 and 19.

The chromatograms from an extraction-analysis sequence of a passive device spiked with lower levels of the standard VOC compounds are shown in Figures 20-22. The chromatogram from the blank analysis of the device before it was spiked is shown in Figure 20. This extraction was conducted for twenty minutes at 125 bar and 65°C. Small contaminant peaks eluted in the retention time windows for chloroform and benzene at approximately 50° and 60°C, respectively. The chromatogram from the actual extraction-analysis of the spiked device is shown in Figure 21. This extraction was also conducted for twenty minutes at 125 bar and 65°C and utilized

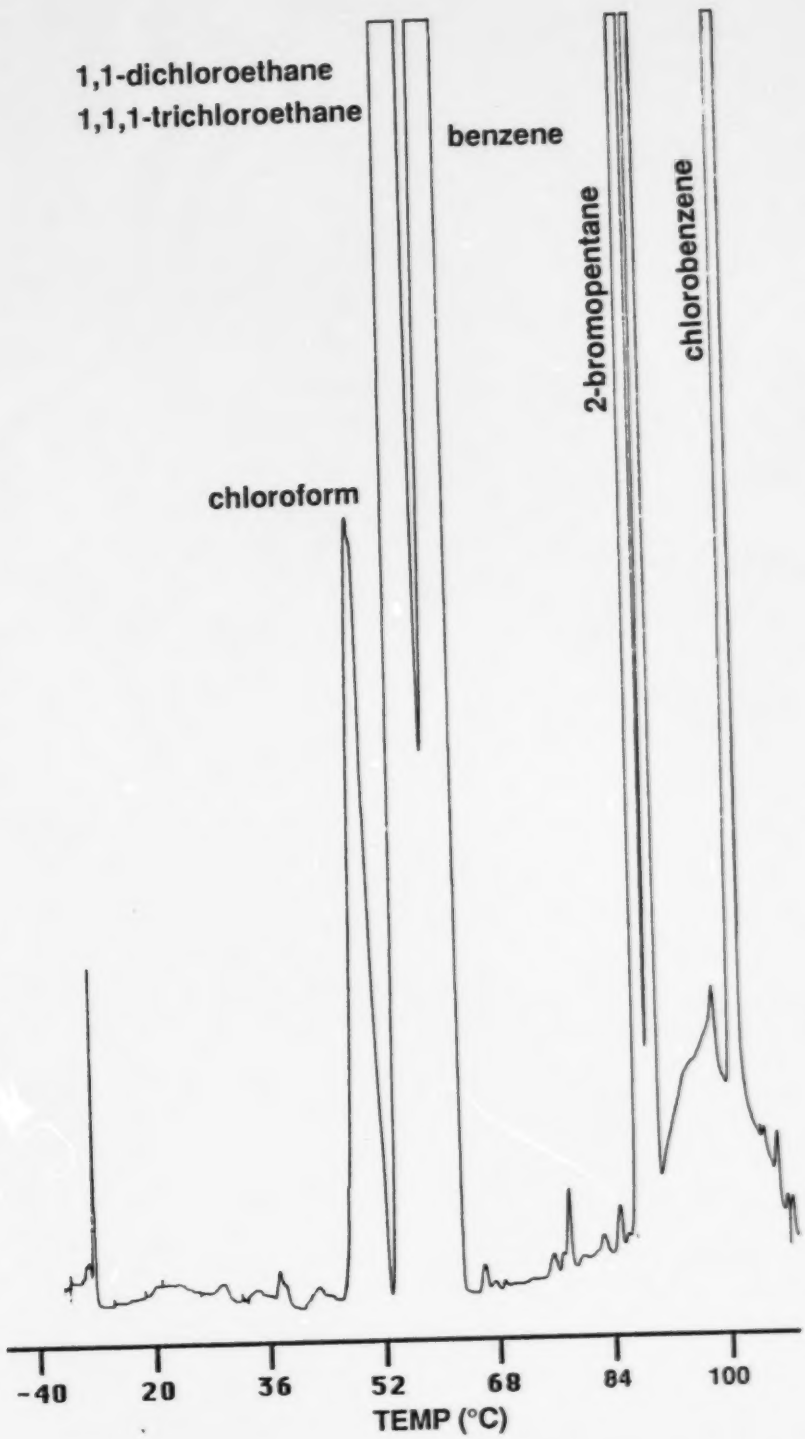

Figure 18. SFE-GC chromatogram from the analysis of a spiked authenic passive sampling device (PSD).

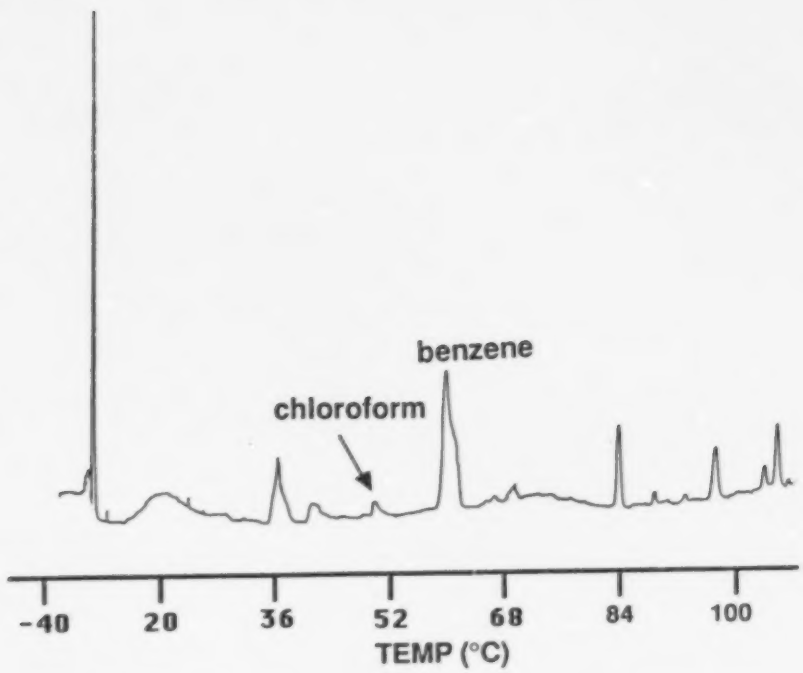

Figure 19. SFE-GC chromatogram from the second analysis of the PSD from Figure 18.

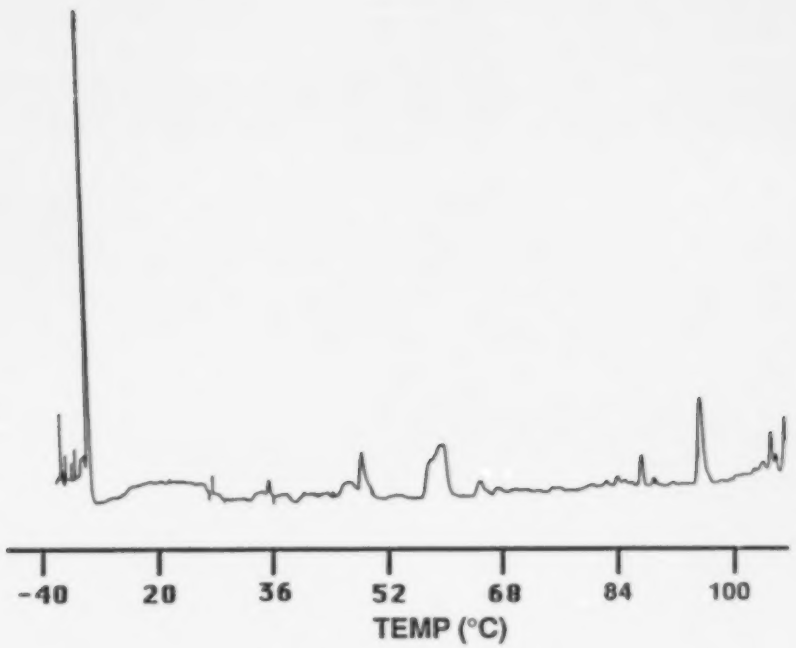

Figure 20. SFE-GC chromatogram of a blank analysis of the PSD prior to spiking with the standard VOC.

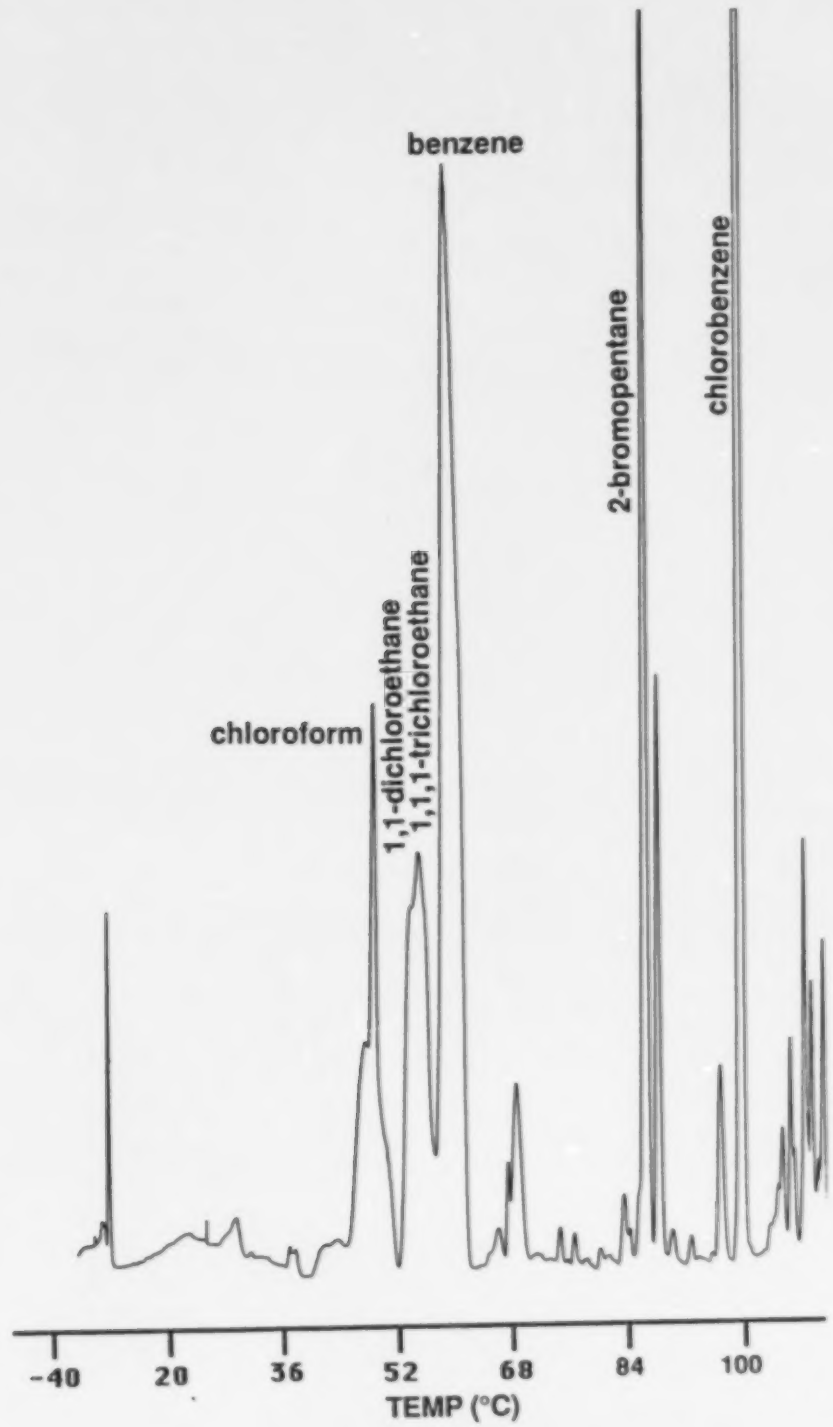

Figure 21. SFE-GC chromatogram from the analysis of the VOC spiked PSD.

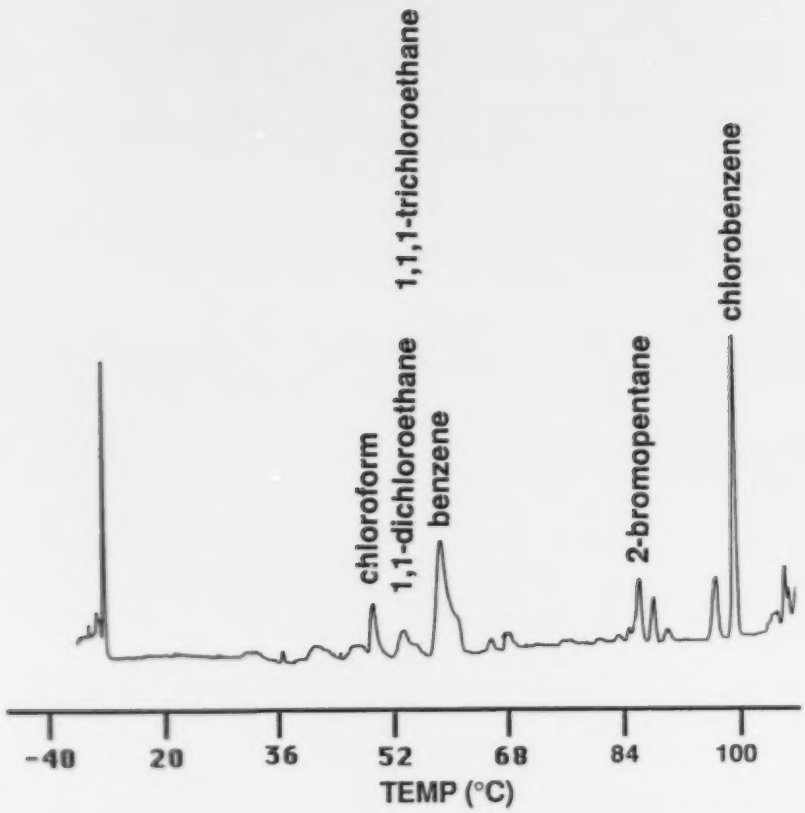

Figure 22. SFE-GC chromatogram from the second analysis of the PSD from Figure 21.

approximately 4 mL of liquid carbon dioxide. Distinctive chromatographic peaks eluted in the appropriate retention time windows for the standard VOC compounds. A possible contaminant peak can be observed eluting with the chloroform peak . The dichloroethane and trichloroethane peaks were only partially resolved due to solute band broadening arising from the more challenging solute focusing requirements from the larger extraction fluid volume. The chromatogram from the second extraction-analysis of the same device is shown in Figure 22. Rather than a completely clean baseline, small peaks corresponding to the retention times of the standard VOC compounds were obtained.

The calculated recovery data and the individual spike levels of the standard VOC compounds for these analyses are listed in Table 5. The spike levels ranged between 79 and 135 ng, and recovery levels ranged from 66 to 172 ng. However, no allowances were made to subtract possible contaminants from the peak integrations. Slightly high quantities were recovered for the less volatile bromopentane and chlorobenzene which suggests that the spiking procedure may not have been totally accurate. The recovery for the dichloroethane was low and the recovery for the trichlorethane was high. However, since these peaks were very poorly resolved it is possible that the integration was skewed. The recovery sums of the two compounds match the sums of the spike levels (the response factors for these two compounds are very similar which makes such a comparison valid).

TABLE 5. RECOVERY DATA FROM A PASSIVE SAMPLING DEVICE

Compound	Spike Level (ng)	Amount Recovered (ng)	Additional Recovered (ng)*
Chloroform	135	148 ± 4	20
Dichloroethane	107	66 ± 3	3
Trichloroethane	121	162 ± 4	1
Benzene	79	97 ± 2	7
Bromopentane	110	137 ± 4	6
Chlorobenzene	100	172 ± 3	10

*from the second analysis

The presence of possible contaminants impaired accurate evaluation of the VOC compound recoveries. It is curious that the sampling device was essentially clean in the blank analysis, yet obvious contaminants were present in the actual analysis and in the second analysis. However, many of these contaminants can be attributed to the spiking procedure. This was verified by several analyses in which clean sampling devices (PSD) were obtained and then removed from the instrument and spiked with ultrapure helium. Subsequent analyses showed the presence of impurities, although the degree of contamination varied widely from apparently similar spiking procedures. The amount of material recovered in the second analysis was relatively low and only ranged from an additional 2 to 11%. In the case of chloroform and benzene, it was not clear if additional material was actually recovered or if additional contaminants were extracted. However, additional quantities of bromopentane and chlorobenzene were clearly recovered. The additional recovery of only low quantities of the standard VOC compounds in the second analysis demonstrated that near quantitative extractions could usually be obtained with a single extraction. It also points out the possible variability between analyses (presumably from spiking) as the analysis described in Figure 18 utilized a device spiked with a higher level of standard VOC compounds, yet they were apparently totally extracted in the first analysis.

Active VOST Sampling Devices

Several analyses of active sampling devices spiked with the standard VOC compounds were also performed. In general, complete extraction of the standard VOC compounds from a device was not obtained with a single thirty minute extraction. Additional quantities were always recovered in the second extraction with higher levels of the less volatile compounds. This behavior was not unexpected since the volume of the VOST devices and quantity of adsorbent was significantly larger than for the other devices. The larger extraction fluid volume (~6 mL liquid) utilized in these analyses created more challenging solute focusing conditions and the chromatographic separation efficiency was degraded for the more volatile compounds.

A typical sequence of chromatograms from the analysis of a spiked active device are shown in Figures 23-25. The chromatogram of a blank analysis of an active device before it was spiked is shown in Figure 23. This extraction was conducted at 125 bar and 65°C for thirty minutes to allow a larger volume of extraction fluid to be utilized for the analysis. Several blank extractions of the device were necessary in order to clean the device and achieve an acceptable background. After extensive extraction, small contaminants were still present near the retention time windows for chloroform and benzene at approximately 50° and 60°C, respectively. The chromatogram of the extraction-analysis of the device after being spiked with approximately 50 ng of each

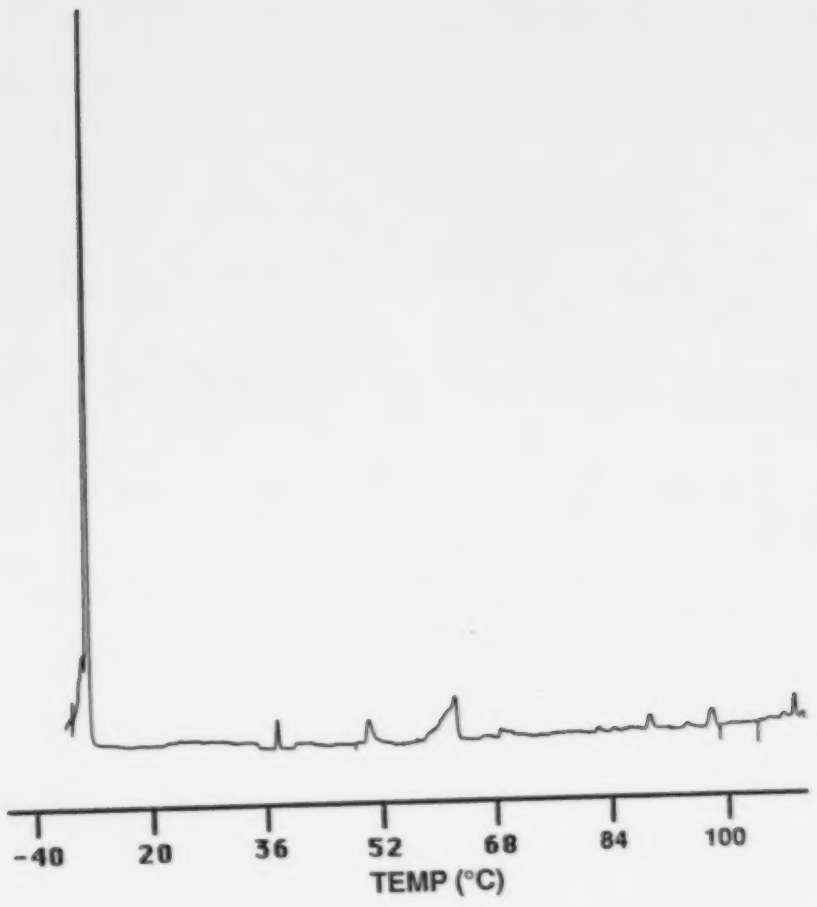

Figure 23. SFE-GC chromatogram from the blank analysis of an active VOST device.

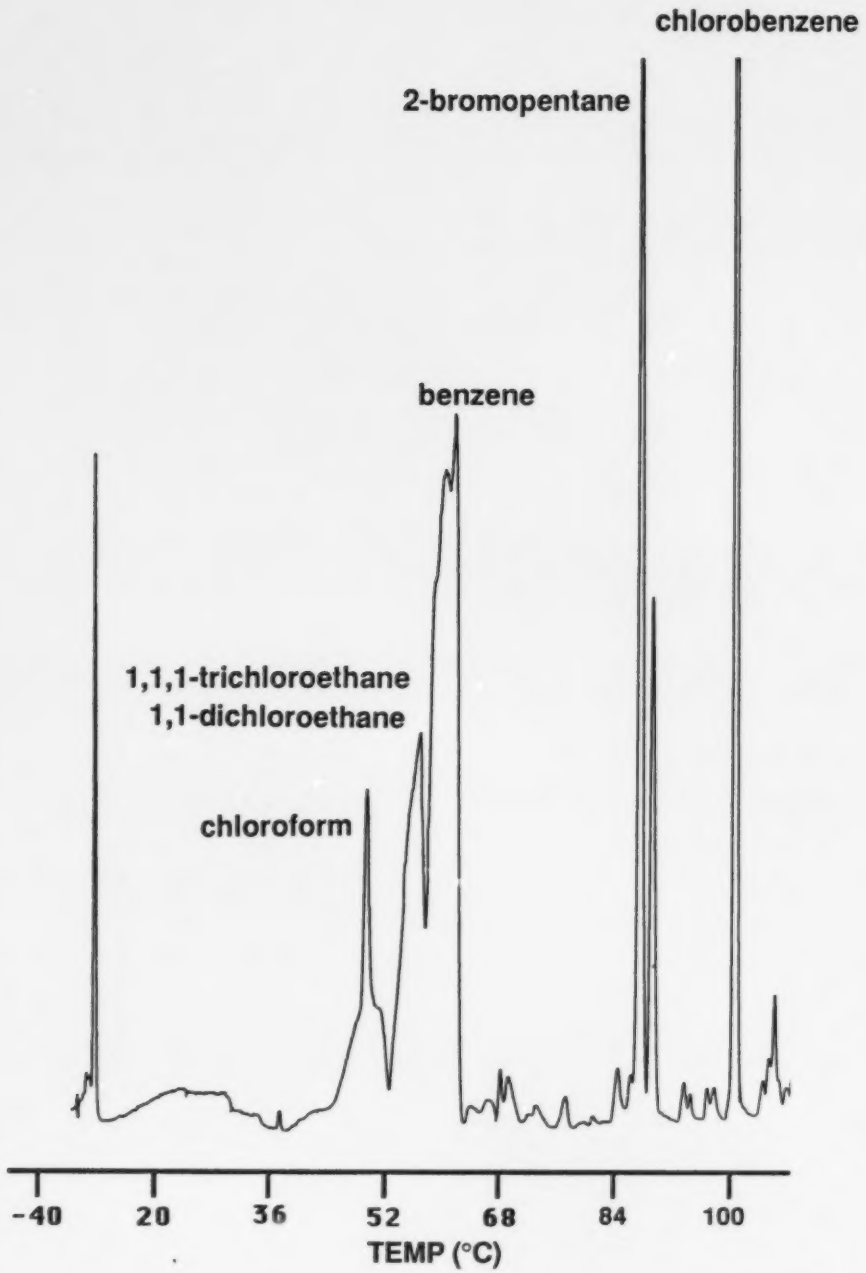

Figure 24. SFE-GC chromatogram from the analysis of an active VOST device.

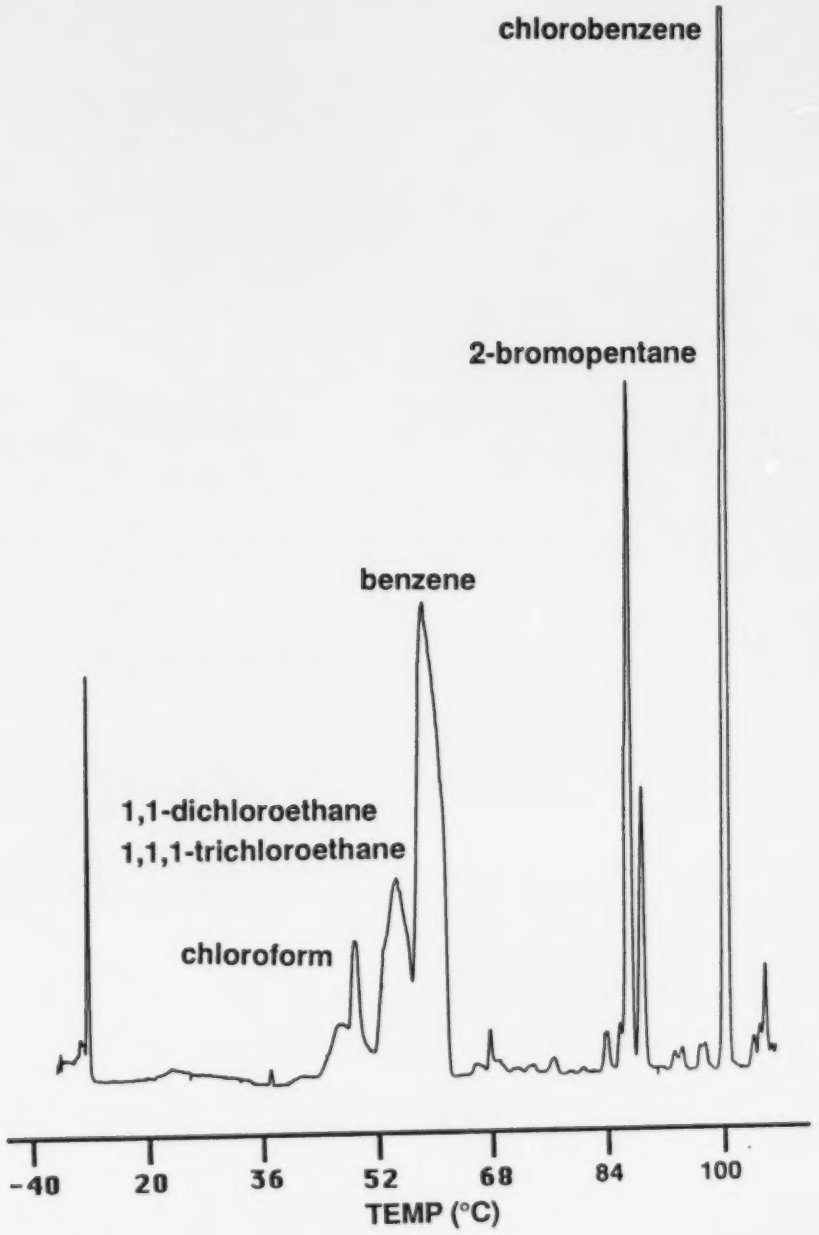

Figure 25. SFE-GC chromatogram from the second analysis of the active VOST device from Figure 24.

compound is shown in Figure 24. The extraction conditions were the same as for the blank analysis. Distinctive chromatographic peaks corresponding to the retention times of the standard VOC compounds were obtained. Again, a contaminant eluted with chloroform and apparently a large contaminant eluted between the unresolved chlorinated ethanes and benzene. The broadened chromatographic peaks and the presence of contaminants prevented rigorous interpretation of this region. It is likely that these contaminants were obtained during the spiking procedure. The chromatogram from the second analysis of the device is shown in Figure 25. A chromatographic profile similar to the first analysis including contaminants was obtained except the intensities of the peaks were generally smaller. A third analysis of the device was relatively clean which suggested that it required approximately sixty minutes of extraction time or 12 mL of liquid fluid volume to achieve complete extraction of the standard VOC compounds (and contaminants) from these devices.

The spiking level and recovery data for the standard VOC compounds from the above analysis sequence are listed in Table 6. The standard VOC compounds were spiked at levels ranging between 44 and 75 ng. Higher recoveries than anticipated were obtained for essentially all of the compounds which can probably be attributed to coeluting contaminants and/or spiking artifacts. Corrected peak areas in which the contaminants were subtracted are also listed for chlorofrom and benzene. The peak areas used to calculate the chloroform levels included only the area above the contaminant peak. For benzene, only the area under the later eluting portion

TABLE 6. RECOVERY DATA FROM AN ACTIVE VOST SAMPLING DEVICE

Compound	Spike Level (ng)	Amount Recovered (ng)	Additional Recovered (ng)*	Total
Chloroform	75	112 ± 3	43 ± 2	155
(without contaminants)		76 ± 2		119
Chloroethanes	128	196 ± 3	102 ± 2	298
Benzene	44	60 ± 2	54 ± 2	114
(without contaminants)		28 ± 1	17 ± 1	45
Bromopentane	61	126 ± 3	72 ± 2	198
Chlorobenzene	56	83 ± 2	86 ± 2	169

*from second analysis

of the peak in Figure 24 was utilized to calculate the recovery level and the same ratio of benzene to contaminant(s) was used for the area of benzene in the peak shown in Figure 25. With these corrections (approximate) the recoveries of chloroform and benzene were close to the spike levels. The chloroethane peaks could also contain contributions from contaminants, but the bromopentane and chlorobenzene peaks were undoubtedly single components. These data illustrate that near quantitative extraction and recovery of the standard VOC compounds could apparently be obtained with two extraction analyses.

The extraction flow rate was increased to allow approximately 400 mL/min gas flow to decrease the extraction time. A chromatogram obtained from the extraction-analysis of an active device spiked with approximately 50 ng of each component using the higher flow rate is shown in Figure 26. This extraction was conducted for thirty minutes at 125 bar and 65°C. A blank analysis of the device prior to spiking verified that it was clean and did not contain residual standard VOC compounds or significant levels of contaminants. This analysis was much cleaner than the one previously described with no apparent contaminants coeluting with the standard VOC compounds. As expected, the large extraction fluid volume decreased the effective solute focusing and the chromatographic peaks of the more volatile components were broadened. No additional quantities of the standard VOC compounds (or contaminants) were recovered from a second extraction-analysis of the device.

The spiking level and recovery data of the standard VOC compounds for this analysis are listed in Table 7. Higher recoveries (200%) than expected were obtained. It is interesting that the recoveries from this analysis and the combined recoveries of the two analyses of the device previously described were similar. The excessive recoveries may have resulted from inaccurate spiking, incomplete previous extractions, and/or inaccurate prediction from the broadened peaks.

TABLE 7. RECOVERY DATA FROM HIGH FLOW EXTRACTION

Compound	Loading Level (ng)	Amount Recovered (ng)
Chloroform	75	136 ± 3
Chloroethanes	128	259 ± 4
Benzene	44	79 ± 2
Bromopentane	61	131 ± 3
Chlorobenzene	56	165 ± 3

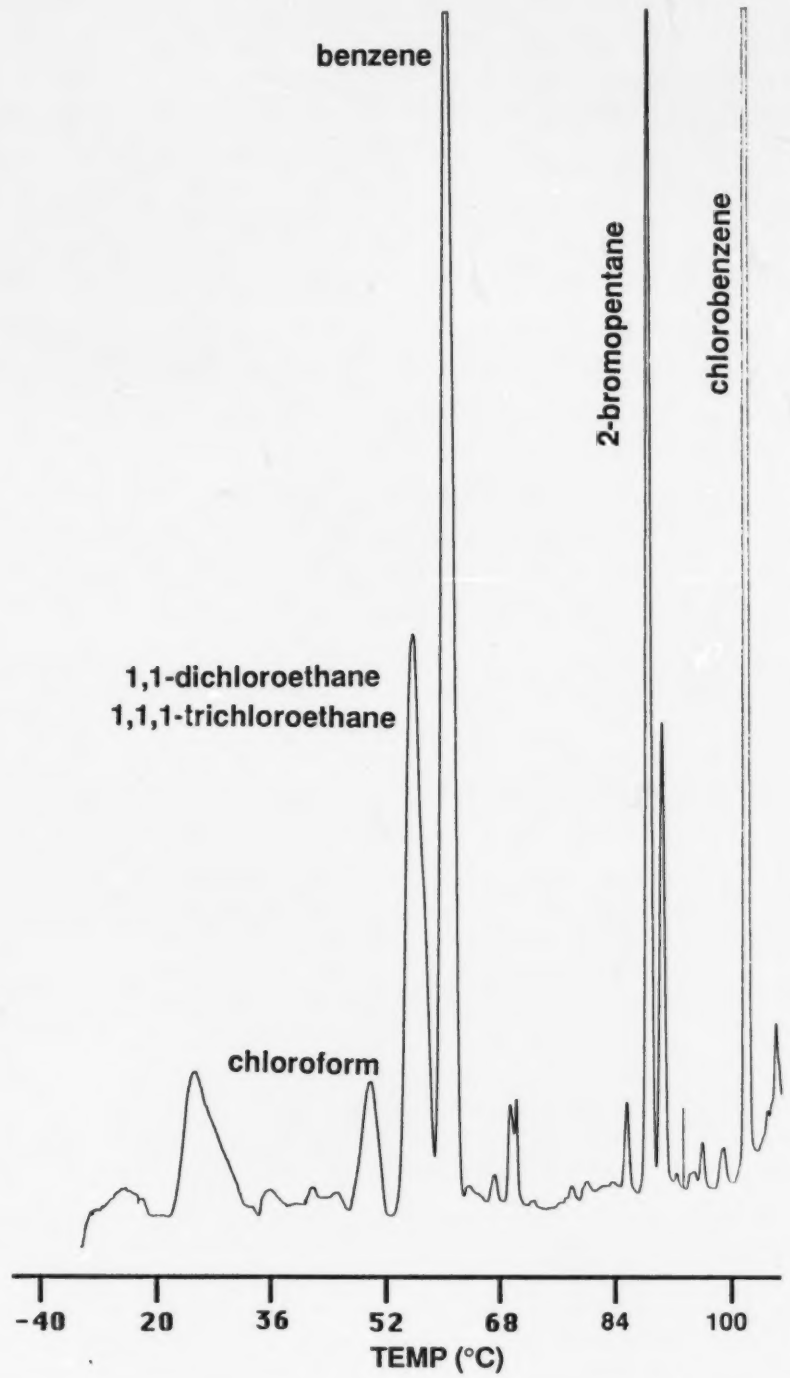

Figure 26. SFE-GC chromatogram from the analysis of an active VOST sampling device using a 400 mL/min extraction gas flow rate.

To test the effects of a different spiking procedure, a clean VOST sampling device was spiked through the extraction fluid exit end rather than through the extraction fluid entrance end. In this way, the extraction was conducted in a back-flush mode. The chromatogram of this extraction-analysis is shown in Figure 27. The extraction was conducted at 125 bar and 65°C for only five minutes with a carbon dioxide gas flow rate of approximately 300 mL/min. No apparent contaminants eluted with the standard VOC compounds and since a relatively low fluid volume was utilized for the extraction (~1.5 mL), the solute focusing was more effective and a more efficient chromatographic separation was obtained. A second ten minute extraction of the device yielded additional quantities of the standard VOC compounds. However, in contrast to the previously described analyses, higher levels of the more volatile compounds were recovered, although the higher levels could have resulted from coeluting contaminants. No additional quantities of the standard VOC compounds were recovered with a third extraction-analysis.

The spiking levels and the recovered quantities of the standard VOC compounds from the two extraction-analyses of the VOST device are listed in Table 8. With the exception of chloroform, only slightly higher levels of the VOC than anticipated were recovered. More reasonable recovery levels might be attributable to more accurate calibration calculations from the more efficient chromatographic peaks. The highest percentage of the total recovered quantities were obtained with the first extraction-analysis. High percentages of the standard VOC compounds were successfully extracted with the significantly lower fluid volume in this analysis due to the spiking method and the back-flush extraction. This is reasonable since only small volumes of gas (0.5 to 1.0 mL) were injected onto the sampling devices during spiking which would have concentrated the standard VOC compounds in the spiked-end of the device. Consequently, the spiking methods used in the previously described analyses would represent the most difficult case for extraction, and the spiking method used for this analysis would represent the best case. An authentically spiked device with a more uniform distribution of solutes on the adsorbent would present an intermediate challenge.

PARALLEL ANALYSES

As an additional evaluation of the supercritical fluid extraction methodology, replicate sampling devices that had been spiked under carefully controlled conditions in an exposure chamber were subjected to parallel analysis using the new methodology and traditional thermal desorption gas chromatography.

Passive Sampling Device

Prior to analyzing the spiked device, blank analyses were conducted on the empty extraction cell to verify that it was clean. The chromatogram of a blank analysis of the PSD extraction cell

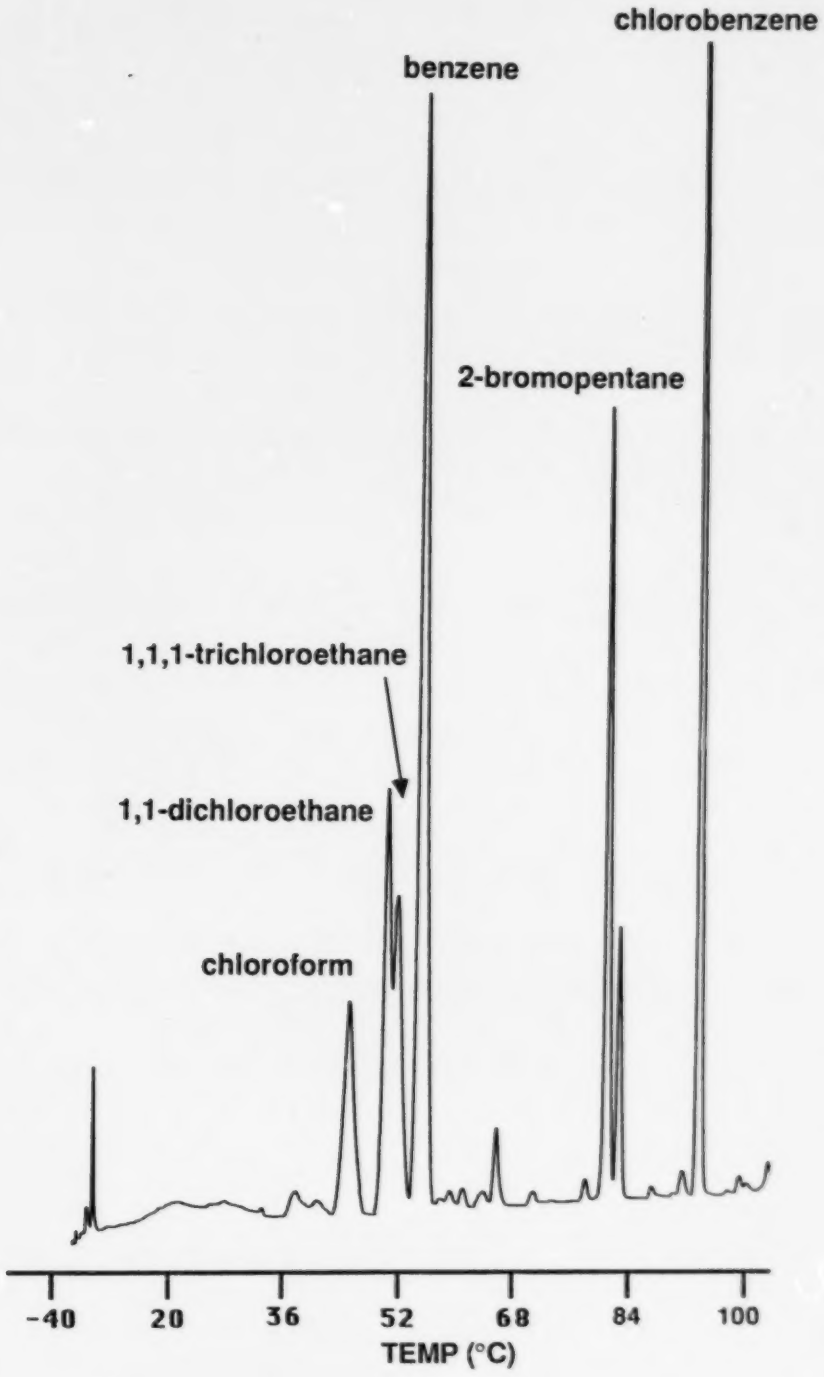

Figure 27. SFE-GC chromatogram from the analysis of an active VOST device that was extracted in a back-flush mode.

TABLE 8. RECOVERY DATA FROM BACK-FLUSH EXTRACTION

Compound	Spike Level (ng)	Amount Recovered (ng)	Additional Recovered (ng)*
Chloroform	75	148 ± 4	10 ± 1†
Dichloroethane	60	68 ± 3	26 ± 2†
Trichloroethane	68	76 ± 3	28 ± 2†
Benzene	44	45 ± 1	21 ± 1†
Bromopentane	61	72 ± 2	10 ± 1
Chlorobenzene	56	67 ± 2	4 ± 1

*from second analysis

†may include coeluting contaminants

is shown in Figure 28. The extraction was conducted for fifteen minutes at 125 bar and 65°C with a 150 mL/min gas flow extraction rate. Several relatively minor contaminants persisted and could not be completely removed. It is likely that these contaminants were extracted from the polymeric O-ring. Without a sampling device inside the cell, the O-ring was exposed to the fluid flow and was more susceptible to extraction. The stair-step baseline early in the chromatogram probably resulted from impurities in the carbon dioxide. The peak which eluted at approximately 60°C was the only contaminant which overlaped the retention time windows of the spiked standard VOC compounds (trichloroethane and benzene).

The spiked PSD was removed from the shipping container and loaded into the extraction cell in a nitrogen flooded glove box to minimize exposure to possible contaminants. After the extraction cell equilibrated to 65°C, a twenty-five minute extraction-analysis was conducted. The chromatogram from this analysis is shown in Figure 29. Numerous chromatographic peaks eluting over the entire analysis range were obtained. Fortunately, two of the peaks corresponded to the appropriate retention times of the spiked standard VOC compounds. Carbon tetrachloride was also spiked on the device, but since flame ionization detection was utilized its response was negligible. (The carrier gas flow rate was varied slightly during the course of this investigation which created corresponding variations in the standard VOC compound elution times. Consequently, the exact elution times vary slightly for different analyses. There is no evidence

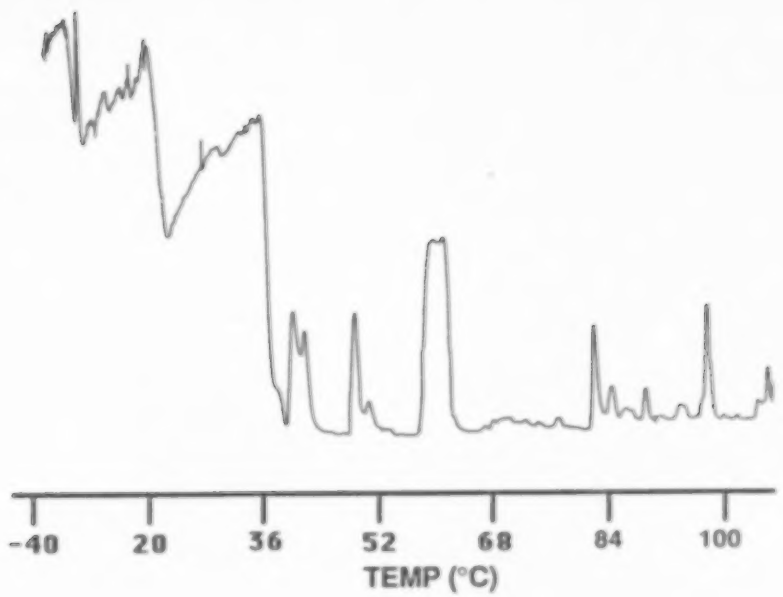

Figure 28. SFE-GC chromatogram from the blank analysis of the empty PSD extraction cell.

Figure 29. SFE-GC chromatogram of the analysis of the exposure chamber spiked PSD.

from this investigation that suggests retention times for sharp chromatographic peaks are any less reproducible than for other capillary gas chromatographic methods.) The relatively large extraction fluid volume (~3.75 mL) prevented highly efficient focusing of the more volatile components resulting in partially resolved and potentially unresolved chromatographic peaks. The chromatogram from a second twenty-five minute extraction-analysis of this device is shown in Figure 30. A much simpler chromatographic profile was obtained, although a wide, partially resolved peak grouping still eluted in the retention time window for the standard VOC compounds. A third extraction-analysis yielded an essentially clean chromatographic profile that was very similar to the blank analysis of the empty cell.

The spiking level and recovery data for the two standard VOC compounds from the different analysis methods are listed in Table 9. The thermal desorption recovery levels were very similar to the spiked levels. However, the recoveries obtained by SFE-GC were higher than anticipated, but could easily be accounted for by coeluting contaminants. Since a contaminant peak from the extraction cell coeluted with the benzene peak, an equivalent area was subtracted from benzene peak area prior to calculating the recovered amount of benzene. The peak cluster eluting at the retention time of benzene in the second analysis (Figure 30) was assumed to be contaminants. Several weeks elapsed from the time the PSD was spiked before it was analyzed which could account for possible contamination. However, previous studies (8) have shown that it is increasingly difficult to recover volatile compounds from Tenax® with elapsed time. SFE-GC analysis apparently removed additional compounds from the sampling device which were not removed by thermal desorption. The presence of potential contaminants coeluting with the standard VOC's prevented rigorous evaluation of the SFE-GC methodology.

TABLE 9. PARALLEL ANALYSIS DATA FOR THE PASSIVE SAMPLING DEVICE

Compound	Spike Level (ng)	Thermal Desorption Recovery (ng)	Supercritical Extraction Recovery (ng)
Trichloroethane	39.6	38.7	$176 \pm 4^{\dagger}$
Benzene	24.8	27.7	$92 \pm 2^{\dagger}$

†may include coeluting contaminants

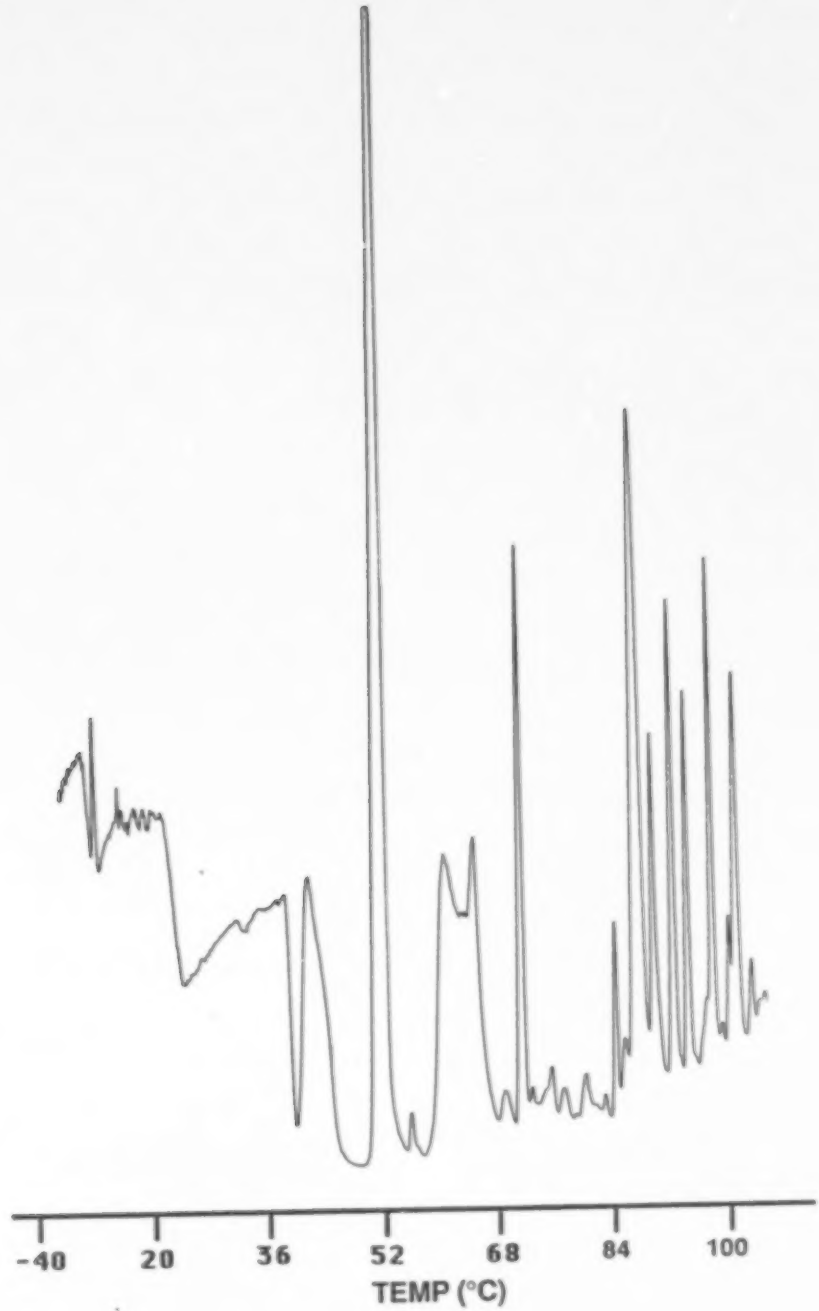

Figure 30. SFE-GC chromatogram of the second analysis of the exposure chamber spiked PSD.

Active VOST Sampling Device

A blank analysis of the empty VOST sampling device extraction cell was also conducted to verify that it was clean. The chromatogram from this analysis is shown in Figure 31. The extraction was conducted for twenty-five minutes at 125 bar and 65°C with a gas flow extraction rate of approximately 200 mL/min. The carbon dioxide used in this extraction was cleaner than used for the passive device described in the last section as evidenced by the flat baseline in the early portion of the chromatogram. The level of contaminants was also much lower with only a relatively small contaminant eluting in the retention time window for the standard VOC compounds at a temperature of approximately 60°C.

The spiked VOST device was uncapped and loaded into the extraction cell inside a nitrogen flooded glove box to minimize contamination. After the extraction cell and device were thermally equilibrated to 65°C, an extraction-analysis was conducted. The same extraction parameters as used for the blank analysis were utilized. The chromatogram from this analysis is shown in Figure 32. Numerous compounds at relatively high levels were eluted over the entire analysis range indicating that the device had become contaminanted or that the supercritical fluid extraction removed additional components from the adsorbent matrix that were not removed by thermal conditioning prior to spiking. Chromatographic peaks were present in the retention time windows for the standard VOC comounds, although it was apparent that contaminant peaks were also present. The chromatogram from the second extraction analysis of the device is shown in Figure 33. A much simpler chromatographic profile was obtained, yet numerous contaminants remained. Surprisingly, a new contaminant overlapping the retention time window of the trichloroethane was present, but otherwise, the first extraction removed the compounds in the retention time window of interest. A third extraction of the device yielded a chromatographic profile similar to the original blank analysis of the extraction cell. The spiking level and recovery data for the two standard VOC compounds from the VOST device using thermal desorption gas chromatography and supercritical fluid extraction gas chromatography are listed in Table 10. The recovery levels obtained using thermal desorption analysis exhibited good agreement with the spiked quantities. A somewhat elevated level of the trichloroethane was obtained, but it is possible that the device was contaminated during removal from the exposure chamber or during analysis preparation. (The ambient laboratory air where these experiments were conducted is known to be contaminated with this compound.) The level of trichloroethane obtained by SFE-GC exhibited better agreement to the spiked level than the level obtained by thermal desorption analysis. The area of the benzene peak was corrected to include only the first peak of the nearly coeluting peak cluster, but a higher than anticipated quantity of benzene was still recovered. The presence of other contaminants likely led to the excessively high recovery level.

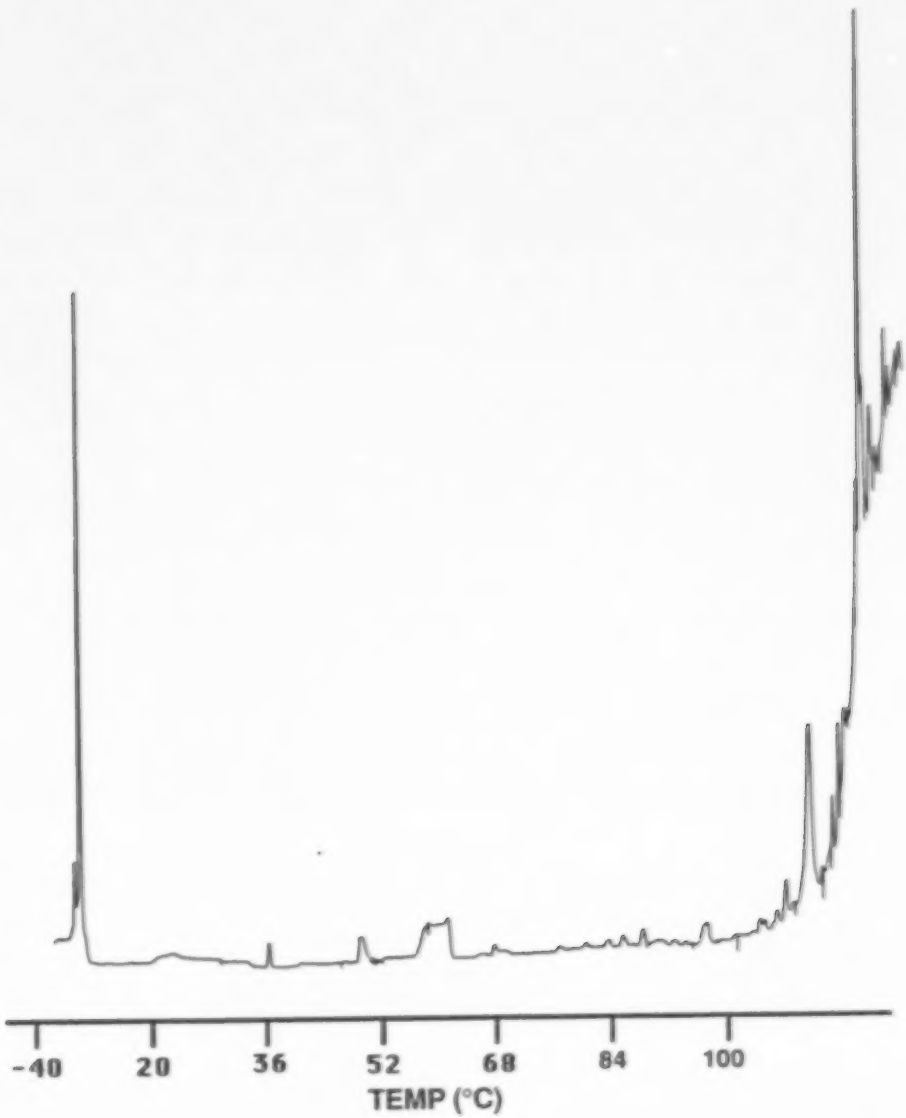

Figure 31. SFE-GC chromatogram from the blank analysis of the empty VOST sampling device extraction cell.

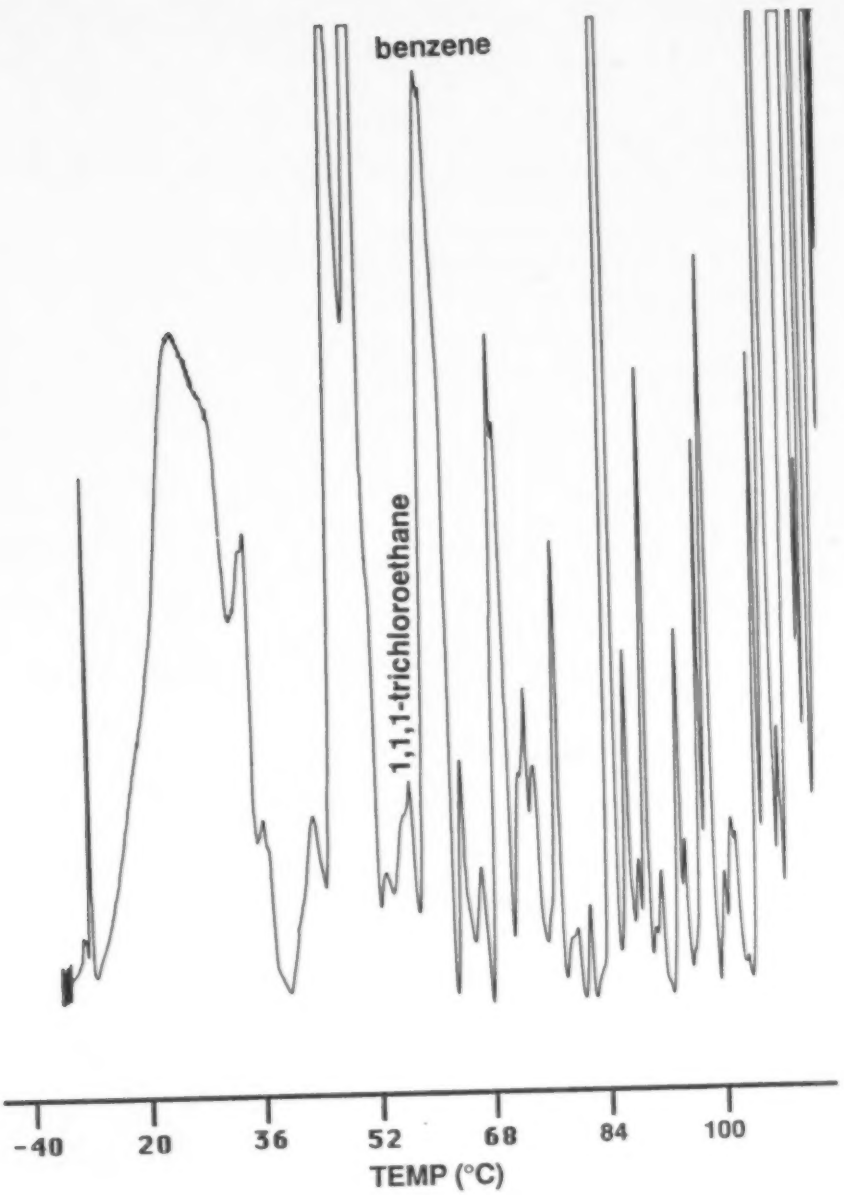

Figure 32. SFE-GC chromatogram of the analysis of the exposure chamber spiked VOST sampling device.

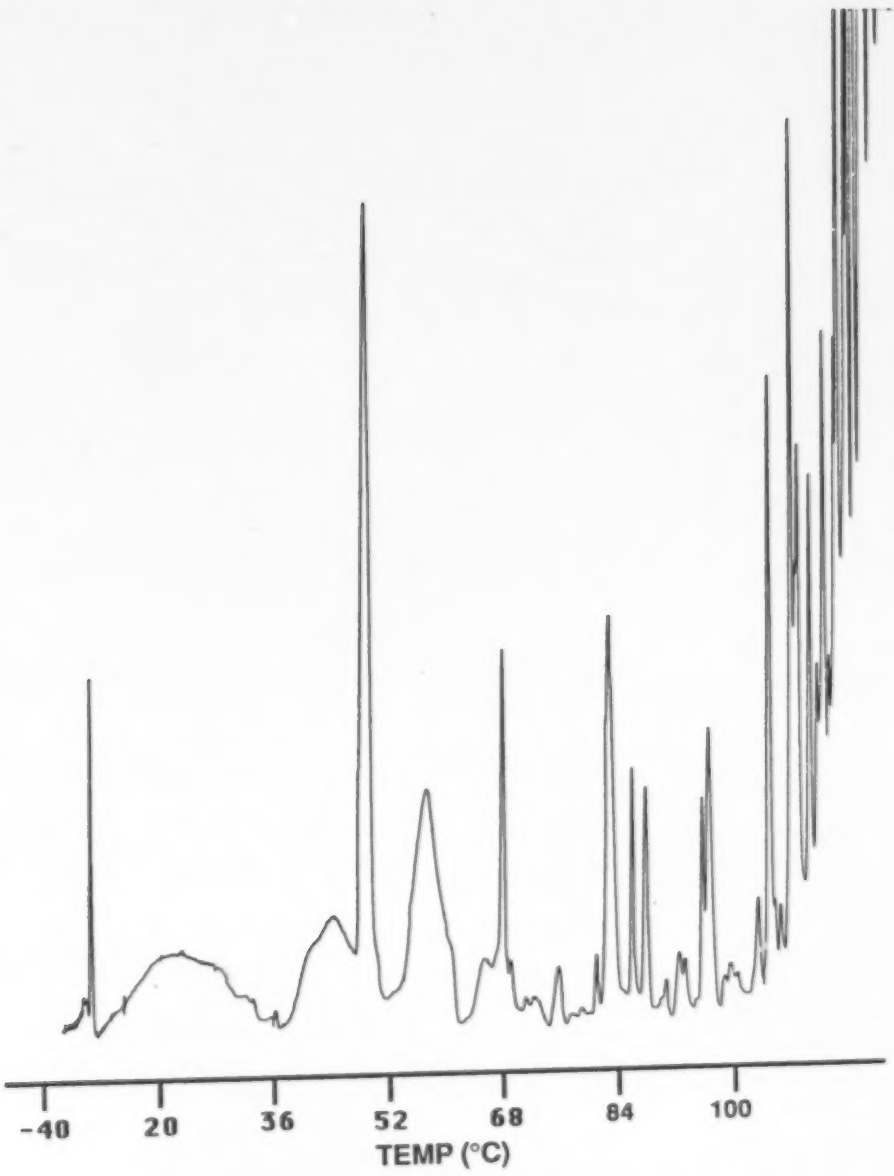

Figure 33. SFE-GC chromatogram of the second analysis of the exposure chamber spiked VOST sampling device.

TABLE 10. PARALLEL ANALYSIS DATA FOR THE ACTIVE VOST SAMPLING DEVICE

Compound	Spike Level (ng)	Thermal Desorption Recovery (ng)	Supercritical Extraction Recovery (ng)
Trichloroethane	39.6	60.0	36 ± 2
Benzene	24.8	26.3	46 ± 1

SEMI-VOLATILE EVALUATION

A preliminary evaluation of the SFE-GC methodology for the analysis of semi-volatile polychlorinated biphenyls was also conducted. Prior to spiking the sampling device, a blank extraction was conducted to ensure that it was free of contaminants. A 0.4 µl volume of a PCB solution containing several congeners at levels ranging betweeen 30 and 90 ppm was liquid spiked on the preliminary Tenax® sampling device. A portion of the solvent was removed by backflushing with high purity helium. The spiked device was then subjected to a ten minute extraction-analysis at 150 bar and 75°C. The chromatogram from this analysis is shown in Figure 34. The expected chromatographic profile was obtained suggesting that the SFE-GC methodology could be easily extended to this volatility range of compounds. No additional compounds were recovered with a second extraction-analysis.

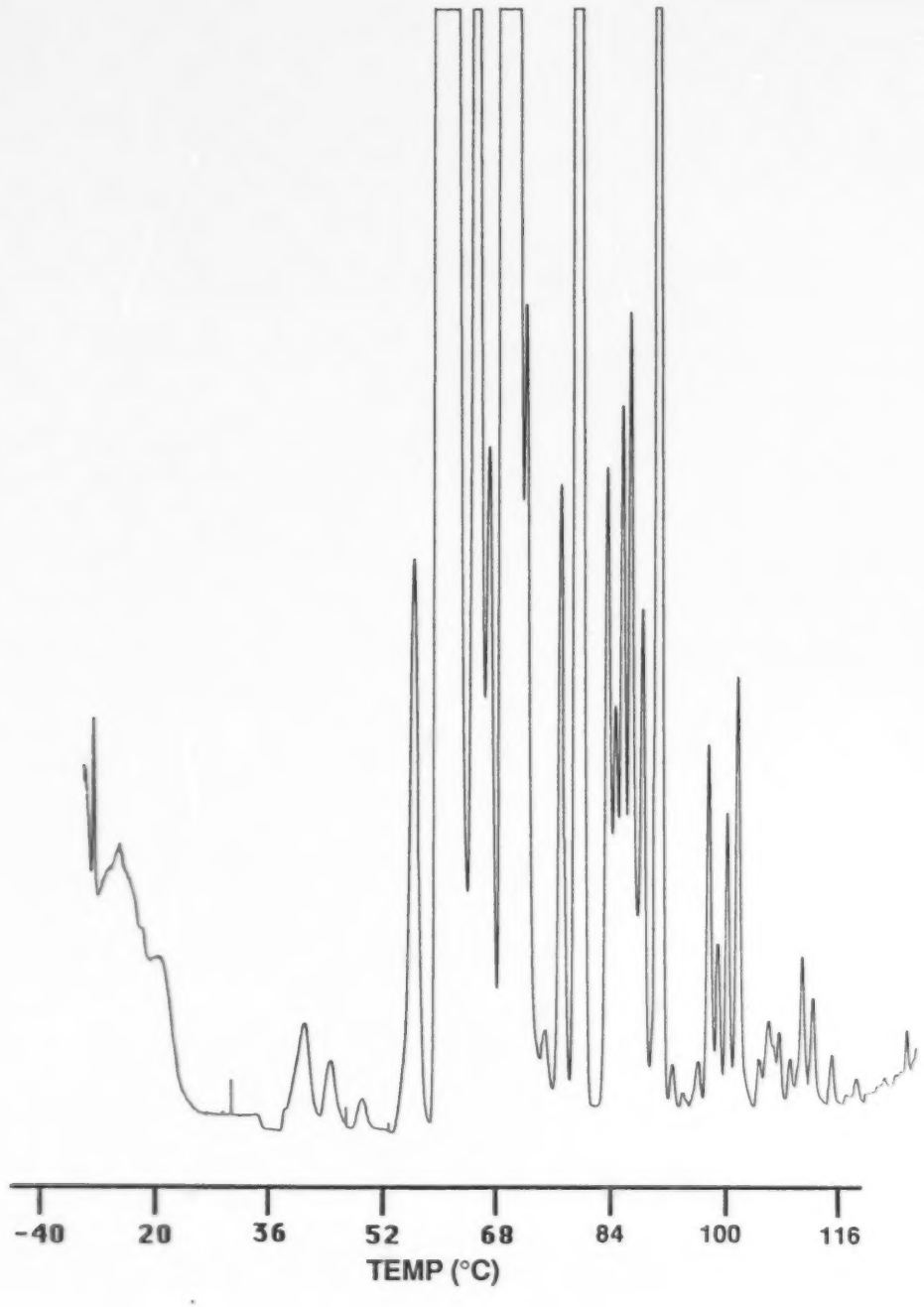

Figure 34. SFE-GC chromatogram of a PCB spiked Tenax® sampling device.

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